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The Raman Spectrum of Sulphuric Acid

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A study was made of the Raman spectrum of sulphuric acid at concentrations varying every five percent from 100 to 5 percent by volume. A dispersion of 10A/mm at 4200A and 15A/mm at 4500A was used. Eight lines were found, which varied gradually in frequency, width, and intensity with changing concentration. Their frequency ranges are 408–432, 561–596, 913–895, 970–973, 980–983, 1031–1051, 1142–1174, 1216–1236, 1352–1332. A gradual change in frequency with concentration was found for a number of the lines. The measurements were checked with a microphotometer.

A NUMBER of investigators have studied the Raman spectrum of sulphuric acid at varying concentrations. This substance is of particular interest because of the presence of molecules and two types of ions. In addition to giving data on the molecular structure, Raman spectra give information regarding the relative abundance of the ions. Nisi[1] found that the lines change in intensity and width with increasing dilution. Ramakrishna Rao[2] and Woodward and Horner[3] reported a frequency shift for some of the lines. The latter found that this shift could be interpreted on the basis of components of slightly different frequency which appeared and disappeared at different concentrations.

In a preliminary report[4] the writers found evidence of a gradual shift rather than components. It was not possible to decide fully whether components existed without a more exhaustive study. Consequently, the Raman spectrum was photographed every five percent from 100 to 5 percent by volume. The conventional set-up with mercury excitation was used. A prism spectrograph was used with a dispersion of 10 A/mm at 4200A and 15 A/mm at 4500A. Lines excited by both 4047A and 4358A were measured as a check on the frequencies. The temperature was kept fairly constant during exposures which varied up to seventy-two hours. Among the difficulties encountered was the continuous background which was especially troublesome for 100 percent acid (F.P. 10.45°C). The broad water band at low concentrations masked some of the lines excited by 4047A. The plates were measured on a comparator and the frequencies calculated from an iron comparison spectrum. For the sharp lines they are accurate to about 3 cm^{-1}; for the broad ones to about 5 cm^{-1}. These frequencies with the widths and intensities are given in Table I. Measurements made with $KHSO_4$ and Na_2SO_4 solutions are given in Table II.

It will be seen from Table I that all of the eight lines have varying characteristics at different concentrations. Line 1 is present everywhere except at very low concentrations. It could not be measured at 100 percent on account of the strong continuous background. The intensity of the nearby mercury lines made the measurements

[1] Nisi, Jap. J. Phys. **5**, 119 (1929).
[2] Ramakrishna Rao, Ind. J. Phys. **8**, 123 (1933).
[3] Woodward and Horner, Proc. Roy. Soc. **A144**, 129 (1934).
[4] Bell and Jeppesen, J. Chem. Phys. **2**, 711 (1934).

TABLE I.

Vol. %	Line 1	2	3	4	5	6	7	8	Mole %
100		562	911			(1142)			100
		(m)	913						
			30						
			6			0			
95	409	561	910	972	1038	1151		(f)	86
	409	(m)	910	971	1038	1153		1352	
	60	60	35		40				
	3	4	6	0	3	0		0	
90	408	565	910	(f)	1038				75
	(f)	(m)	910	970	1038	(f)		(f)	
	60	60	35		40				
	3	4	5	0	4				
85	412	570	910	973	1035				65
	416	(m)	909	(f)	1033	(f)		(f)	
	60	60	35		40				
	3	4	5	0	4				
80	417	577	907		1035				58
	(f)	(f)	904		1032	(f)		(f)	
	60	60	40		40				
	3	4	5		5				
75	418	579	905		1034				51
	421	(f)	906		1032	(f)		(f)	
	60	60	40		40				
	3	4	4		5				
70	424	582	903		1034				45
	421	(f)	901		1031	1157	1216	1341	
	60	60	40		40				
	3	4	4		5	0	0	0	
65	423	583	897		1035				39
	(419)	(f)	900		1031	(f)	(f)	(f)	
	60	60	45		40				
	3	4	4		5				
60	425	586	899		1036				34
	(f)	(f)	899		1036	1166	1221	1345	
	60	60	45		40				
	3	4	4		5	0	0	0	
55	426	585	897	982	1036				29
	(f)	(f)	897	(f)	1034	(f)	(f)	(f)	
	60	60	50	15	40				
	3	4	3	1	5				
50	426	588	897	982	1038				25
	425	589	(w)	983	1038	1172	1234	1341	
	60	60	50	20	40				
	3	4	3	2	5	0	0	0	
45	425	588	897	981	1038				22
	(f)	(f)	(w)	983	1037	1174	1232	(f)	
	60	60	50	20	40				
	3	4	3	3	6	0	0		
40	427	589	897	982	1042				19
	(423)	587	(w)	982	1039	1164	1227	1332	
	60	60	55	20	35				
	3	4	2	4	6	0	0	0	
35	427	590	896	982	1043				16
	(f)	(f)	(w)	980	1042	1172	1234	(f)	
	60	60	55	20	35				
	3	4	2	5	6	0	0		
30	427	593	896	982	1047				13
	431	(596)	(w)	980	1045	1172	1223	1334	
	60	60	55	20	30				
	3	4	2	6	6	0	0	0	
25	425	594	897	982	1047				10
	429	(w)	(w)	980	1048	1168	1233	1337	
	60	60	60	20	30				
	3	4	1	6	6	0	0	0	
20	(429)	592	897	981	1048				7.8
	(f)	(w)	(w)	982	1045	(f)	(f)	(f)	
	60	60	60	20	25				
	3	4	1	6	6				
15	(432)	592	(895)	983	1050				6.0
	(f)	(w)	(w)	981	1047	1168	1236	(f)	
	60	60	60	20	25				
	3	4	0	6	6	0	0		
10	(f)	592	(895)	983	1051				3.6
		(w)	(w)	981	1050				
		60	60	20	20				
		4	0	6	6				
5				982	1051				1.8
				(w)	1047				
				20	20				
				6	6				

(f) too faint to be measured on comparator
(w) masked by water band
(m) masked by mercury line
( ) uncertain

The columns refer to the several lines observed. For a given concentration the first number is the $\Delta\bar{\nu}$ from 22,938 cm^{-1} (4358A), the second the $\Delta\bar{\nu}$ from 24,705 cm^{-1} (4047A), the third the width of the line in cm^{-1}, and the fourth the intensity.

at low concentrations uncertain. This line is broad and of constant intensity at all concentrations. It seems to increase in frequency as is shown in Fig. 1. Line 2 is similar to line 1. It has the same width and is a little more intense. It appears at all concentrations from 100 to 10 percent and gradually increases in frequency. The excitation from 4047 coincides with the 4142 mercury line at high concentrations, but is easily separated at low concentrations. The similarity of lines 1 and 2 may mean that they originate from the same scatterer.

Line 3 is the most intense line at 100 percent and practically disappears for very dilute solutions. It broadens noticeably and decreases in frequency for low concentrations. Its great intensity at 100 percent seems to indicate a connection with the molecule. Line 4 appears first at about 55 percent and increases in intensity with dilution. The frequency remains constant as far as can be determined, and the line is uniformly sharp wherever it appears. Because its frequency checks with the strongest line observed in sulphate solutions (Table II), it has been ascribed to the $S\overline{O}_4$ ion. This would indicate the presence of a large number of $S\overline{O}_4$ ions from 35 to 5 percent. From 95 to 85 percent a weak 971 cm^{-1}

TABLE II.

	Mole %	$\bar{\nu}$	$\Delta\bar{\nu}$	
$KHSO_4$	2.2	21,955	983	(4)
		21,890	1048	(5)
Na_2SO_4	0.4	21,958	980	(5)
		23,724	981	(4)

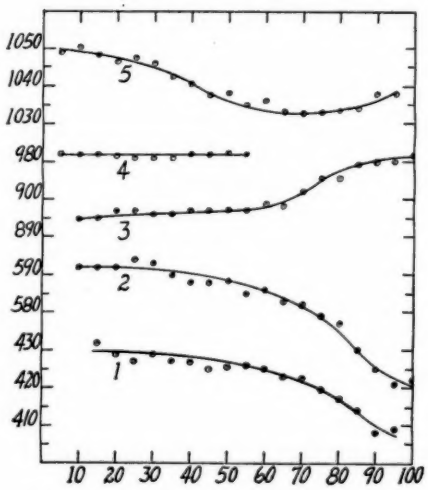

FIG. 1. Average frequencies of the five most intense lines plotted against the concentration in volume percent.

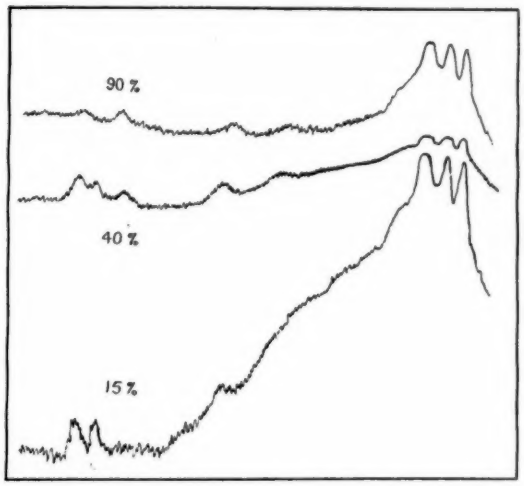

FIG. 2. Reproduction of microphotometer curves of lines excited by 4358A.

line is found. It is entirely absent at low concentrations. It should not be confused with the 981 cm^{-1} line. The strong continuous background may mask it at 100 percent. Line 5 does not appear at 100 percent, but shows up faintly in pure acid which has been exposed to the air for only a few hours. Since this is in agreement with the strongest line found in acid sulphate solutions (Table II), it has been ascribed to the $HS\overline{O}_4$ ion. The intensity variation shows that this ion is present in solutions containing only a trace of water and that it is present in great abundance from 45 to 5 percent. Its frequency seems to decrease slightly and then increase. Sufficient data are not available to determine whether this frequency shift is also characteristic of the 1048 acid sulphate line.

Line 6 is never strong but appears at practically all concentrations. A shift of 1146 cm^{-1} has been reported[5] for SO_2 solutions. Line 7 was not found at 100 percent, but at intermediate concentrations it is slightly more intense than line 6. Woodward and Horner found evidence for this line in their microphotometer curves. Line 8 appears very faint at a number of concentrations. It is in approximate agreement with the 1340 cm^{-1} SO_2 line.[5] The frequency shift of lines 6, 7 and 8 is open to question on account of the difficulty in measuring such weak lines. They could be measured best in the region excited by 4047 because of the absence of background. The 3450 cm^{-1} water band first appears at 80 percent. It broadens and increases in intensity with dilution. Siva Rao[6] has found a gradual decrease in frequency for this band, going from 3468 cm^{-1} at 32 percent to 3424 cm^{-1} for pure water. A careful search failed to show any lines corresponding to S−H or O−H bonds in sulphuric acid.

If each line consists of components whose intensities depend upon the concentration there should be a particular concentration favorable to the simultaneous appearance of two components. Photographs taken every 5 percent have failed to reveal this. If they do exist their frequency differences must be much less than that previously reported. On the other hand a gradual shift is indicated for some of the lines. This is shown in Fig. 1. In most cases the change is most rapid around 85 percent.

Microphotometer measurements were made over the range studied. Three representative curves are reproduced in Fig. 2. The symmetrical shape of all the lines makes the existence of any components doubtful. A study of all the microphotometer data seems to verify the frequency, width and intensity variations reported in Table I.

The writers wish to thank the Physics Department of Johns Hopkins University for the use of their microphotometer.

[5] Bhagavantam, Ind. J. Phys. 5, 59 (1930).

[6] Siva Rao, Ind. J. Phys. 9, 195 (1934).

Raman Spectra of Some Molecules of the Pentatomic Type

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Raman spectra of a number of organic compounds containing a neopentyl group have been obtained. Among these is tetramethyl methane-d_1. The spectrum of this compound shows the various types of isotope effects to be expected for a polyatomic molecule. It is also apparent from the spectrum that the vibrations of tetramethylmethane-d_1 are less degenerate than the vibrations of tetramethylmethane. The spectrum of tetramethylsilicon has 5 lines in the internal vibration spectrum. The explanation for the existence of this extra line is probably the same as that given by Fermi in the case of CCl_4.

INTRODUCTION

THE study of organic chemistry has furnished us with an enormous number of different species of molecules whose geometrical structure has been determined quite satisfactorily on the assumption of a static molecule. In dealing with the vibrations of the atoms in a molecule the chemist's static model is invaluable. From this model we are able to predict the number of possible types of vibrations and the degree of degeneracy in the case of symmetrical molecules.

The molecules which have been investigated in the present work have been chosen because of the various degrees of simplicity introduced into their vibration spectrum because of their symmetry properties.

The title of this paper is in one sense a misnomer, since no pentatomic molecules were investigated. Cross and Van Vleck[1] have treated the ethyl halides as though they were triatomic molecules with a fair degree of success. If we consider a methyl group for example as a single atom, then the molecules in the present investigation which will be discussed can be considered to be of the pentatomic type.

The molecules whose Raman spectrum has been investigated were tetramethylmethane-d_1; silicon tetramethyl; 2,2,4-trimethylpentene-3; 2,2,4-trimethylpentene-4; 2,2,4-trimethylpentane; 2,2,4,4-tetramethylpentane; 3-hydroxypentane and 2-chloropentane. The structural formulae of these compounds and a schematic diagram of their Raman spectra are shown in Table I.

The experimental technique employed in the present work has been described by one of us[2] previously. The spectrograph had a dispersion of 14A/mm at λ4500. However, in the case of silicontetramethyl and 2,2,4,4-tetramethylpentane the spectrograph was fitted with an $F=9$ lens (dispersion 25A/mm at λ4500). The use of the faster spectrograph in the above two cases was necessary because of the small amounts of these compounds available and the comparative feebleness of the scattered light.

The 2,2,4-trimethylpentene-3 and 2,2,4-trimethylpentene-4 were samples of the compounds separated by Whitmore and Wrenn[3] and were considered to be in a high state of purity. The 2,2,4-trimethylpentane, 3-hydroxypentane and 2-chloropentane were furnished us by F. C. Whitmore from a stock of very carefully purified compounds. In the case of the compounds mentioned above samples of approximately 15 cm³ size were used to obtain the Raman spectrum.

Tetramethylmethane-d_1

A 4 cm³ sample of material which consisted of approximately a 50–50 mixture of tetramethylmethane and tetramethylmethane-d_1 was used in this case to obtain the Raman spectrum. The preparation† of this material has been described elsewhere.[4]

* From a dissertation submitted by D. H. Rank in partial fulfilment of the requirements for the Ph.D. degree at The Pennsylvania State College.

[1] Paul C. Cross and J. H. Van Vleck, J. Chem. Phys. **1**, 350 (1933).

[2] D. H. Rank, J. Chem. Phys. **1**, 572 (1933).

[3] Whitmore and Wrenn, J. Am. Chem. Soc. **53**, 3136 (1931).

† A preliminary report on the preparation and the spectrum of tetramethylmethane-d_1 was given by one of us (R) in conjunction with Mr. G. H. Fleming before the Florida meeting of the American Chemical Society.

[4] Whitmore, Fleming *et al.*, J. Am. Chem. Soc. **56**, 749 (1934).

2,2,4,4-tetramethylpentane

A 4 cm³ sample of this material[5] which was prepared and purified by Dr. F. C. Whitmore and Dr. H. A. Southgate was used to obtain the Raman spectrum.

Tetramethylsilicon

This material was specially prepared for us by Dr. F. W. Breuer of the Chemistry Department and had the following physical constants:

$$Nd = 1.37315 \text{ at } -5.5°C,$$
$$\text{b.p. } 26\text{–}26.5°C \text{ at } 720 \text{ mm}.$$

We have tabulated the frequencies for tetramethylmethane along with that of the mixture of tetramethylmethane and tetramethylmethane-d_1 for comparison purposes. The frequency shifts are given in cm^{-1}. The numbers in parentheses are eye estimates of the relative intensity of the lines.

Tetramethylmethane

335 (10)	414 (3)	733 (20)	925 (15B)	1252 (20B)
1455 (15)	2712 (5)	2745 (3)	2794 (3)	2864 (7)
2892 (5)	2911 (10)	2937 (3)	2955 (7B)	

Tetramethylmethane-d_1+tetramethylmethane

283 (3)	338 (6)	418 (4)	723 (20)	736 (20)	819 (6)
930 (15)	1223 (4)	1251 (15)	1302 (3)	1377 (3)	1395 (3)
1453 (15)	2179 (5)	2521 (2)	2714 (6)	2779 (3)	2796 (3)
2870 (10)	2900 (5)	2917 (15 V.B)		2959 (15 V.B)	
2916 (3)	2961 (5 V.B)				

Silicon tetramethyl

202 (20B)	239 (15B)	598 (20)	696 (15B)	863 (10B)
1264 (10B)	1427 (15B)	2905 (10B)	2963 (10B)	

2,2,4-trimethylpentene-3

133 (2B)	202 (2)	300 (2)	327 (8)	506 (2)
568 (8)	760 (20)	820 (4)	924 (10)	940 (2)
1027 (4)	1071 (6)	1159 (4)	1204 (6)	1257 (4)
1357 (4)	1386 (10)	1395 (6)	1450 (15)	1466 (8)
1667 (15)	2903 (10)	2948 (15B)	3000 (15B)	

2,2,4-trimethylpentene-4

124 (4B)	190 (2)	294 (4)	315 (4)	387 (4)
461 (2)	561 (10)	685 (15)	765 (20)	829 (6)
894 (4)	910 (8)	936 (8)	999 (2)	1049 (2)
1101 (2)	1155 (8)	1207 (6)	1240 (10)	1268 (2)
1297 (2)	1328 (2)	1413 (15)	1450 (12B)	1648 (15)
2906 (6)	2947 (10B)	2996 (10)	3021 (6)	

2,2,4-trimethylpentane

302 (2B)	512 (4)	745 (20)	788 (4)	828 (4)
902 (8)	929 (8)	1101 (6)	1167 (4B)	1207 (6)
1250 (6B)	1358 (4)	1458 (10B)	2905 (10B)	2943 (15B)
2998 (15B)				

2,2,4,4-tetramethylpentane

274 (2)	425 (2)	557 (2B)	736 (20)	862 (2)	881 (5)
930 (5B)	1250 (10B)	1450 (10)	1480 (5)	2915 (10B)	2966 (10B)

[5] Whitmore and Southgate (preparation of this compound to be published).

3-Hydroxypentane

400 (3)	472 (2)	763 (3B)	829 (2)	857 (4)
965 (4B)	1013 (2)	1038 (4)	1128 (2)	1276 (2)
1307 (2)	1363 (2B)	1454 (10B)	2918 (10)	2974 (10B)
3005 (5)				

2-Chloropentane

295 (2B)	342 (3)	380 (3)	399 (3)	426 (3)
442 (3)	511 (2)	536 (3)	612 (10B)	672 (4B)
846 (5)	873 (5)	921 (2B)	1029 (3)	1049 (3)
1087 (3)	1124 (2)	1275 (3)	1309 (3)	1451 (10B)
2914 (5)	2967 (7B)	3013 (4)		

Discussion of Results

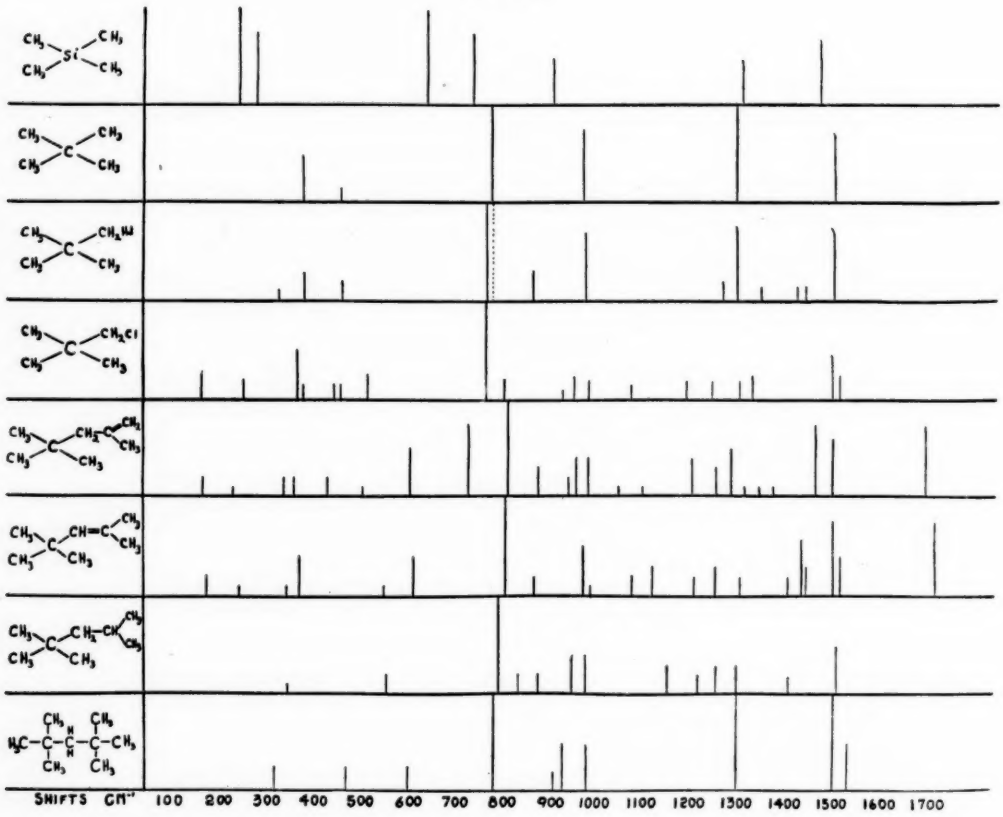
The vibrations of pentatomic tetrahedral molecule are discussed in detail in Born's *Optik*.[6] As is well known a symmetrical pentatomic molecule has four distinct vibrational frequencies. In the case of CCl_4 for which complete data are available the multiplicities and depolarizations have been completely determined. The lowest frequency has a multiplicity of two and the next lowest a multiplicity of three. The totally symmetric vibration is single while the highest frequency has been shown to be a triple vibration. In the infrared spectrum only the two triply degenerate frequencies make their appearance while in the Raman spectrum all four of these fundamental vibrations are observed. The doublet and triplet lines in the Raman spectrum show a depolarization of $\frac{3}{4}$. However, the totally symmetric single vibration shows a depolarization of zero.

The Raman spectrum of tetramethylmethane shows six lines in the frequency interval 0 to 1500 cm^{-1}. Of these the four lowest can be ascribed to the four fundamental frequencies of a symmetrical pentatomic molecule if we are privileged to consider a CH_3 group as a single atom. The infrared spectrum of tetramethylmethane is not available so there is no direct evidence to allow us to choose the triply degenerate frequencies with certainty. However, there seems to be no good reason why we should not assign the multiplicities of 2, 3, 1, 3 in this molecule for the four vibrations in the order of increasing frequency as has been shown to be true in the case of CCl_4. There can hardly be any doubt as to the fact that this assignment is correct in the case of the higher two of the four frequencies.

The frequencies 1252 and 1455 cm^{-1} must undoubtedly be ascribed to vibrations of deformation of the methyl groups in which the hydrogens

[6] Max Born, *Ein Lehrbuch der Electromagnetischen Lichtheorie*, p. 553.

TABLE I.



are directly involved. Regarding the multiplicity of these vibrations we can say practically nothing except that they are probably highly degenerate, since in the case of derivatives of tetramethylmethane we obtain a large number of lines in this region which definitely cannot be ascribed to splitting up of the fundamental "framework" vibrations.

The most striking feature seen on the plates showing the Raman spectrum of these molecules containing the "neopentyl" group is the high intensity and the extreme sharpness of the line which varies from 721 to 765 cm^{-1} depending on the compound. The 598 cm^{-1} line of silicontetramethyl shows exactly the same characteristics. In the symmetrical compounds no lines of a sharpness comparable to this one are found. In the case of CCl_4 Langseth[7] has found the 458 cm^{-1} line to be exceedingly sharp as is attested by his beautiful photographs in which he shows the resolution of the lines which correspond to molecules containing 1 and 2 atoms, respectively, of chlorine 37. It is well known that the usually termed name Raman lines is a misnomer and that actually a Raman line is an unresolved band caused by the overlapping rotational structure. It appears from the plates that the lines corresponding to the totally symmetrical vibration consist only of the closely spaced rotational branches in contradistinction to the other broader lines where apparently the more widely spaced branches were also allowed. The existence of this single extremely sharp line in the spectrum of these compounds shows definitely that rotational structure rather than perterbation of the energy levels by surrounding molecules in the liquid is responsible for the breadth of the other lines.

The spectrum of silicon tetramethyl shows the same degenerate character of the vibration spectrum as tetramethylmethane. The internal vibrations of this molecule lie at somewhat lower frequencies than is the case with tetramethyl-

[7] A. Langseth, Zeits. f. Physik **72**, 350 (1931).

methane. The frequencies 1264 and 1427 cm^{-1} which are undoubtedly associated with the methyl group vibrations, remain substantially the same as in tetramethylmethane. In the case of lead tetramethyl apparently, according to Duncan and Murray,[8] this is no longer true and these vibrations are degraded to lower frequencies as well as the internal vibrations. In the case of silicontetramethyl we obtain a fairly intense line at 863 cm^{-1} which does not fit into the scheme of vibrations for a pentatomic molecule. It seems quite probable that the same explanation as that used by Fermi[9] for CCl_4 would hold in this case. If this explanation would be true we must assume that the highest triply degenerate frequency of the internal vibration spectrum is still unknown but very close to the sum of 202+598 cm^{-1} which produces a splitting resulting in the production of the two lines, 696 cm^{-1} and 863 cm^{-1} instead of the single line ordinarily to be expected.

Tetramethylmethane-d_1

The results in the case of this molecule are not entirely unambiguous. About 50 percent of the molecules were ordinary tetramethylmethane and it is not possible to say whether all the lines found in tetramethylmethane are absent in the deutero derivative or not. The slight differences in the frequencies of lines known to be due to tetramethylmethane as measured on the two sets of plates are in some cases due to experimental error but in other cases may be due to superposition of the two sets of lines from the two different compounds present. For this reason it seems difficult to speculate with any degree of certainty concerning the splitting up of the internal vibrations of the molecule due to partial destruction of the symmetry by the substitution of a deuterium atom for a hydrogen atom. However, the spectrum clearly shows that the vibrational degeneracy of the tetramethylmethane-d_1 molecule is not as complete as that of the tetramethylmethane molecule. The lines 1223, 1302, 1377, 1395 cm^{-1} are almost certainly due to the splitting up of the highly degenerate frequencies which lie at 1252 and 1455 cm^{-1}, respectively, in the tetramethylmethane molecule. The totally symmetrical vibration exhibits an isotope effect of 13 cm^{-1}. The line appearing at 2179 cm^{-1} is undoubtedly a vibration of the type commonly called C–H "stretching vibrations" in which the deuterium atom forms part of a simple oscillator and is vibrating against part or all of the molecule with little or no interaction with other vibrations. The line at 2521 cm^{-1} is probably of the same type but with the added restriction of interaction with other vibrations of the molecule.

In the case of monochlorotetramethylmethane, 2,2,4-trimethylpentene-3, 2,2,4-trimethylpentene-4, and 2,2,4 trimethylpentane the large number of lines shows that the degeneracy of the tetramethylmethane molecule has been practically completely removed. An inspection of Table I seems to show a grouping of lines of varying separation which might be traced to the fundamental degenerate frequencies of tetramethylmethane.

Conclusion

This series of compounds has been studied with the idea in mind to treat them as pentatomic molecules. The spectrum of the symmetrical molecules tetramethylmethane and silicon tetramethyl has been satisfactorily explained by considering the vibrations of a pentatomic molecule. The spectrum of tetramethylmethane-d_1 shows the various types of isotope effects expected for a polyatomic molecule. It also shows that the substitution of a deuterium atom for a hydrogen atom in tetramethylmethane partially destroys the dynamic symmetry and as a consequence partially removes the vibrational degeneracy. The large number of lines appearing in the spectrum of the other tetramethylmethane derivatives shows practically complete removal of vibrational degeneracy.

Acknowledgments

We wish to express our appreciation to Dean F. C. Whitmore of the School of Chemistry and Physics for making this rare series of compounds available for this investigation. We are also deeply indebted to Dr. F. W. Breuer for the special preparation of the tetramethylsilicon which we have used.

[8] A. B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[9] E. Fermi, Zeits. f. Physik **71**, 259 (1931).

Scattering of X-Rays by Polyatomic Liquids. *n*-Heptane

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(Received March 5, 1935)

A Fourier integral analysis of Katzoff's data for the x-ray scattering of *n*-heptane gives not only the arrangement of molecules in the liquid, but also the most probable distances within the single molecule. It is shown that the molecule consists of a zigzag carbon chain. Adjacent molecules are somewhat oriented and increase in temperature makes a more random condition. The Fourier integral theorem is shown to be valid even though the function for which it is used does not converge within the limits of the data. The distribution function is used to calculate the intensity, giving a fair agreement with the experimental values.

RECENT publications[1, 2] in the field of x-ray scattering by liquids have led the writer to the questions:

(a) How much information concerning the structure of single molecules may be obtained from liquid scattering data?
(b) Is the use of the Fourier integral theorem valid for data extending over a small range of $\sin\theta/\lambda$?

The data of Katzoff[3] for *n*-heptane have permitted calculations that furnish definite answers to the questions. These data are particularly excellent for they are taken with monochromatic x-rays, the absorption in the sample is determined, and they extend over a large angular range.

THEORY

Zernike and Prins[4] and Debye and Menke[5] have developed equations for the x-ray scattering of atomic liquids in terms of a distribution function. Warren[1] and Zachariasen[2] have applied these in slightly modified form to the scattering of molecular liquids having atoms of equivalent scattering power. The Fourier integral theorem is used to solve these equations for the distribution function.

The fundamental scattering equation

$$I_{(\text{obs.})}/NTF^2-1=(1/K)\int_0^\infty (q(r)/r)\sin Krdr \quad (1)$$

gives on transformation

$$q(r)=(2r/\pi)\int_0^\infty K(I_{(\text{obs.})}/NTF^2-1)\times\sin KrdK, \quad (2)$$

where:

$I_{(\text{obs.})}$ is the observed scattering, corrected for absorption, polarization and incoherent scattering;
N is the number of irradiated atoms;
T is the scattering per electron;
F is the atomic scattering factor for the given value of K;
K is $4\pi\sin\theta/\lambda$, where θ is half the scattering angle and λ is the wavelength;
$q(r)$ is the number of atoms in excess of the average lying at distance r Angstroms from a given atom;
$I_{(\text{obs.})}/NTF^2$ is for brevity denoted by E, in keeping with common usage.

Eq. (2) is identical in meaning with Eq. (2) of Katzoff's paper, since the average number of atoms at r is $4\pi r^2\rho$ (ρ is atoms per A^3).

In practice the data do not extend to infinity, nor does $K(E-1)$ converge at the largest obtainable values of K. The results, however, show that no great error is introduced by integrating from $K=0$ to $K=2\pi$.

METHOD OF CALCULATION

The E-curve is determined as shown in Fig. 1. Katzoff's intensity curves for *n*-heptane were replotted to a convenient scale and the calculated F^2 and incoherent scattering curves drawn to the same scale. At the point $s(2\sin\theta/\lambda)=1$, it may be assumed that the atoms scatter independently and that the observed scattering is thus the sum of the independent coherent scattering plus the modified scattering. The point $s=1$ was chosen because on the theoretical gas scattering curve it lies half-way between a maximum and a minimum. The procedure is not very exact for large s values because of uncertainty both in the F^2 and

[1] B. E. Warren, Phys. Rev. **44**, 969 (1933).
[2] W. H. Zachariasen, Phys. Rev. **47**, 277 (1935).
[3] S. Katzoff, J. Chem. Phys. **2**, 841 (1934).
[4] F. Zernike and J. A. Prins, Zeits. f. Physik **41**, 184 (1927).
[5] P. Debye and H. Menke, Physik. Zeits. **31**, 797 (1930).

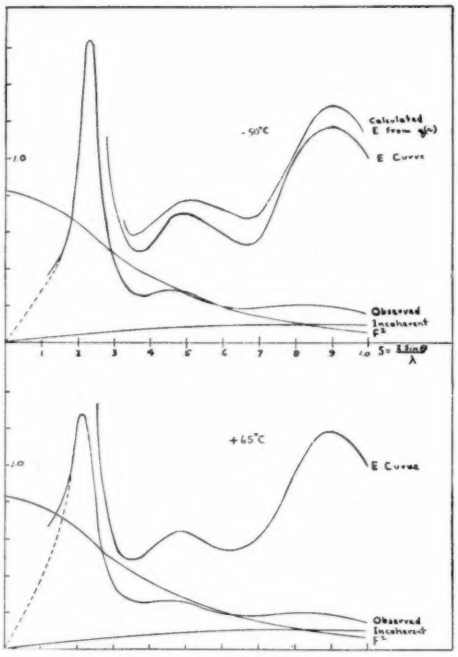

FIG. 1. Scattering curves for *n*-heptane (Katzoff); E curves and E curve calculated from $q(r)$ curve.

the experimental curves, but subsequent calculations showed that the results were chiefly due to portions of the scattering curve at smaller s values where the accuracy is greater. James and Brindley's[6] F values were used for carbon and hydrogen. In the F^2 curve the values are for $C^{=}$ $(Z=8)$ and the hydrogen is neglected. The E curves are obtained by dividing the experimental curves by the F^2 curves. Since both are in the same units, E is in absolute units.

Integration of Eq. (2) was carried out in 0.25A steps for values of r from 0.25A to 15A. This laborious calculation was materially shortened by the use of a Coradi rolling sphere harmonic analyzer.[7] The function $K(E-1)$ was plotted against K, (Fig. 2) and expressed as a Fourier series by tracing with the harmonic analyzer. The resulting expression for $K(E-1)$ was multiplied by $\sin Kr$ and each term integrated from $K=0$ to $K=2\pi$. The corresponding $q(r)$ curves are shown in Fig. 3.

[6] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

[7] Available through the courtesy of Professor Henry Schultz of the Department of Economics, University of Chicago.

DISCUSSION

The $q(r)$ curves have unexpectedly sharp peaks at 1.4, 2.5, and 3.8A. These peaks are due to the outer parts of the scattering curve, where the molecules scatter quite independently, and they undoubtedly show within experimental limits the most probable distances within a single molecule. This is verified by the slight change with temperature and by calculations made with an arbitrarily drawn $K(E-1)$ curve which minimized the fluctuations at large K values. This curve (Fig. 2A) follows the $-50°$ curve to $K=\pi$ and diverges in the range where the experimental uncertainty is greatest. It gives the distribution function of Fig. 3A. The peaks appear at the same r-values, but are much less pronounced. Since the experimental uncertainty is probably not as great as shown in the arbitrary curve the true distribution function probably lies between the two curves.

The $q(r)$ peaks at larger distances show the concentration of scattering matter in adjacent molecules. The peak for the lower temperature curve is at $r=4.5$ to 6.5A, with a mean value of 5.25 to 5.5A. This distance is somewhat greater than the mean diameter of the molecule because of the distribution of scattering atoms along the length of the adjacent molecule. At the higher temperature the peak extends outward, giving a mean value of about 5.75A. Elevation of the temperature has only increased the amplitude of the molecular vibration and given a more disorderly arrangement.

The most probable distance (a) of scattering atoms may be more directly determined, as shown by both Zachariasen and Warren, by application of the Ehrenfest-Keesom equation

$$\lambda/2 \sin\theta(\max) = d_{\text{Bragg}} = 0.814a.$$

The value so calculated from the major peak of the scattering curve is the same as given by the $q(r)$ curve. Application of this equation to the second and third peaks gives distances of 2.54 and 1.43A, respectively.

The radial distribution obtained does not imply the assumption of a structure for the liquid. Although they may be in random motion and orientation with respect to a given point, two adjacent

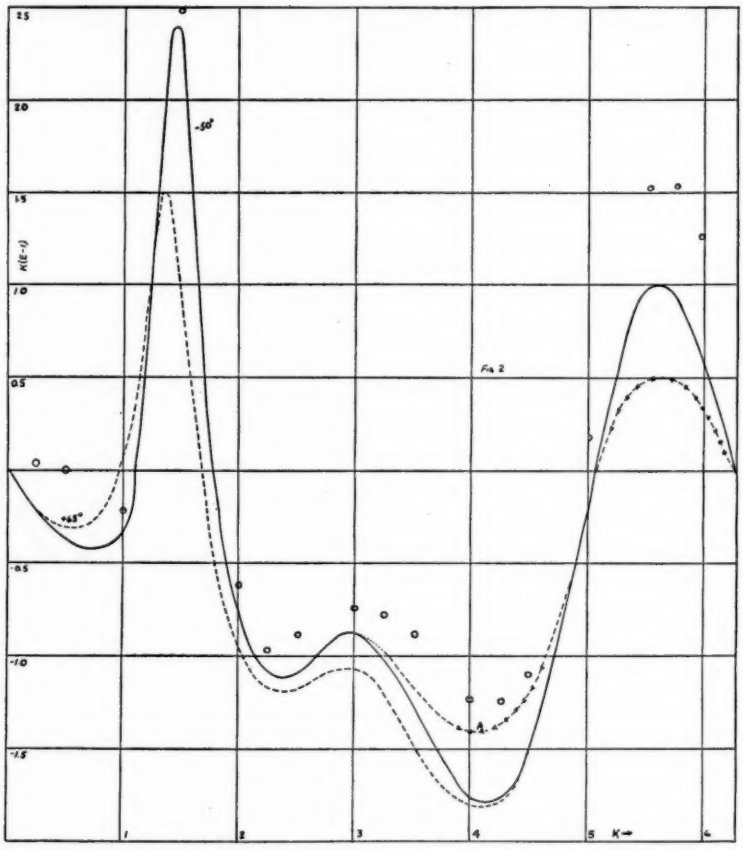

FIG. 2. $K(E-1)$ curves for n-heptane ——— 50°; ····· 65°; * * * * smoothed data for −50°; o o calculated from $q(r)$.

molecules must be in a somewhat parallel arrangement because of their shape and size. The free space in a liquid is probably small in comparison to the volume occupied by the molecules, and there is not sufficient space for adjacent molecules to turn endwise with respect to one another. Two widely separated molecules may, however, have any orientations.

The packing of the molecules seems to be in a hexagonal arrangement for it appears from the $q(r)$ curve that each molecule has on the average about six neighbors. This is deduced from the area under the peak, about four atoms. Since the average number of atoms at a distance of 4.5 to 6.5A is about twenty-five (as computed from molecular volume) the total number at this distance is about twenty-nine. This would require about six neighboring molecules.

The results of the present calculation may also be interpreted by the cybotactic theory, for if the arrangement were crystalline the distribution function would be about the same as found. Warren and Gingrich[8] have applied the Fourier integral analysis to the scattering from a solid, sulfur, and obtain a distribution similar to that given by a liquid.

The question as to the validity of the use of the Fourier integral theorem was raised because the data do not extend beyond $K=2\pi$ while the integration must be performed in the limits $K=0$ to $K=\infty$. An attempt to find the magnitude of the probable error was made by calculating the intensity function from the $q(r)$ curve. The portion of this from $r=0$ to $r=4\pi$ was expressed as a Fourier series by the harmonic analyzer and the integration of Eq. (1) was performed. The calculated $K(E-1)$ curve is shown by the circles of Fig. 2 and by the upper E curve

[8] B. E. Warren and N. S. Gingrich, Phys. Rev. **46**, 368 (1934).

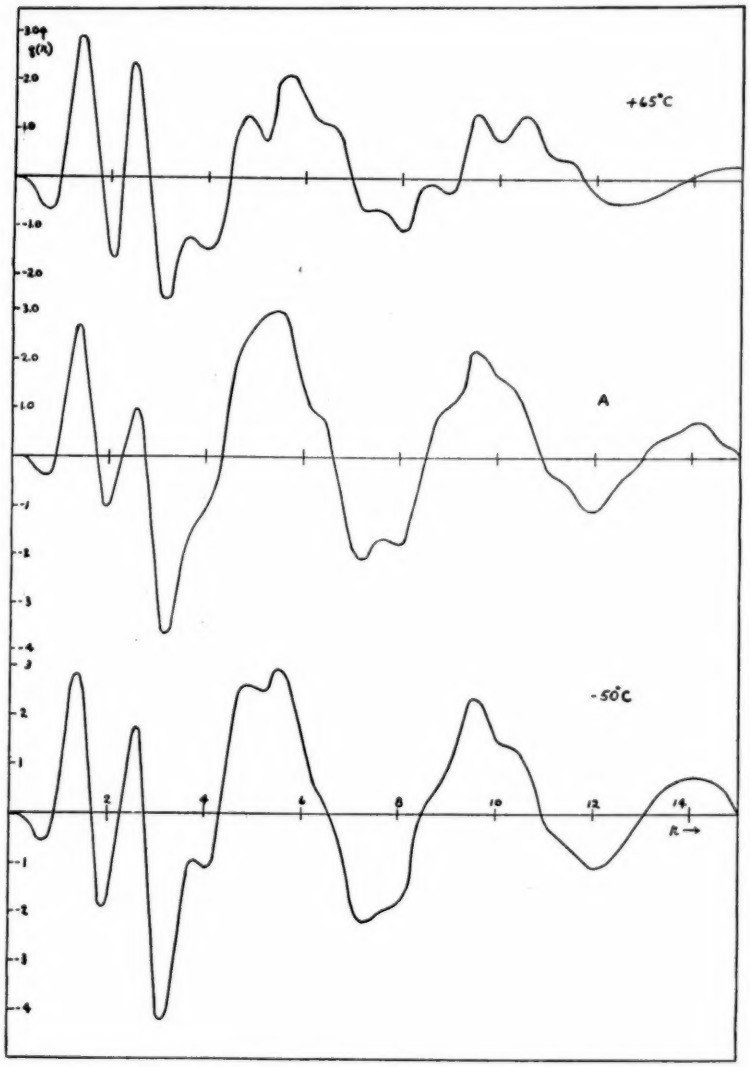

FIG. 3. Distribution function for *n*-heptane. The $q(r)$ values give the number of atoms in excess of the average at radial distance r.

of Fig. 1. The calculated intensity is somewhat too high by a nearly constant factor but the shape of the curve is the same as the original and the peaks are at the same positions. The small fluctuations at large r values in the $q(r)$ curve may be due to the finite integration. (Another possibility is in the extrapolation of the scattering curve to zero scattering angle.)

The success of the calculation in giving both the inner and outer structures of the liquid emphasizes the importance of the Fourier integral method of analysis and shows the need for more quantitative data extending to large angles.

The writer desires to express his thanks to Professor W. H. Zachariasen for his helpful criticisms.

The Far Ultraviolet Absorption Spectra of Formaldehyde and the Alkyl Derivatives of H_2O and H_2S

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(Received March 10, 1935)

The absorption spectra of formaldehyde and of compounds of the type HOH, ROH, ROR and HSH, RSH, RSR have been observed in the region 2300–1000A. An analysis of the spectrum of formaldehyde yields a value of 10.83 ± 0.01 volts for the first ionization potential of the C=O bond and about 164 Cal./mole for the strength of this bond. The spectra of the alkyl derivatives of H_2S are all shown to be shifted to the long wavelength region relative to those of H_2O. Rough estimates of their ionization potentials are given and the influence of dipole moment on the ultraviolet absorption spectra and ionization potentials of polyatomic molecules is discussed.

THE author has for some time been investigating the absorption spectra of various organic molecules in the far ultraviolet. Up to the present, work of this nature has been done almost exclusively with fluorite spectrographs by using the H_2 continuum. The instruments used in this work are two vacuum grazing incidence spectrographs which have dispersions of 11–9A/mm and 2.7–2.0A/mm, respectively, in the region 2000–1000A. The source of the continuum was a Lyman discharge tube of the type developed by Collins and Price.[1] The use of this continuum in preference to the H_2 continuum enabled the absorption to be followed down to 1000A. Both gratings were of glass and each was ruled with 30,000 lines to the inch. The radius of curvature of the smaller was 40 cm and that of the larger was two meters. The path lengths of the absorbing columns in the two spectrographs were about 35 and 150 cm, respectively.

The gas to be investigated is led into the body of the spectrograph through a fine capillary and pumped out through the main evacuating pump. The pressure of the gas used in obtaining these absorption spectra is usually of the order of a tenth of a millimeter. The author has shown that in a large number of cases[2] the bands obtained under these conditions consist of various electronic series with a superimposed vibrational pattern which go to a limit agreeing fairly well with the ionization potential of the molecule as obtained by electron impact.

A photograph of the absorption spectrum of formaldehyde taken under high dispersion is given in Fig. 1. The gas was obtained by heating paraformaldehyde. The absorption is very strong and most of the bands appear at a pressure of 0.1 mm in a path length of 1.5 meters. On account of the diffuseness of the bands the analysis is rather difficult. It is however plain that the bands converge to a limit around 1150A.

TABLE I. *Comparison between calculated and observed values for the frequency differences between successive series members in formaldehyde.*

n	Intensity	Wave number	Difference between successive members (cm^{-1}) Obs.	Calc.
		SERIES (i)		
2	10	71600		
			7820	7766
3	10	79420		
			3300	3281
4	8	82720		
			1650	1687
5	8	84370		
			980	980
6	7	85350		
			600	619
7	6	85950		
		SERIES (ii)		
2	10 D	64270		
			13400	10667
3	10 D	77670		
			4080	4142
4	9 D	81750		
			2060	2028
5	8	83810		
			1140	1142
6	8	84950		
			700	705
7	7	85650		
			470	466
8	5	86120		

* Commonwealth Fellow.

[1] G. B. Collins and W. C. Price, Rev. Sci. Inst. **5**, 423 (1934).

[2] W. C. Price, Phys. Rev. **45**, 843 (1934); **46**, 529 (1934); Phys. Rev. **47**, 444, 510 (1935).

The strong bands can be classified into two electronic series. The frequencies of their members are given in Table I. As most of the members are a few Angstroms broad, the measurements can only be relied upon to within 50 wave numbers. Also, they all contain a considerable amount of fine structure due to the low moment of inertia of the molecule about the CO axis. Even with the high resolution used here, little could be done with this and the measurements given correspond to the center of the band. The higher members of (i) and (ii) conform fairly well to the following Rydberg series:

(i) $\nu_0^n = 87{,}830 - R/(n+0.60)^2$,

(ii) $\nu_0^n = 87{,}710 - R/(n+0.30)^2$, $n = 2, 3, 4$ etc.

An idea of the accuracy with which these formulas represent the series may be obtained from an inspection of Table I.

The first member of series (ii) is somewhat off the Rydberg formula. This may probably be accounted for by the presence of a dipole in the CH_2 group which means that the electron is escaping in a field given approximately by

$$\nu = e/r_1 + (p \cos\theta)/r_2^2$$

"p" being the moment of the dipole, "r_2" the distance of the electron from the center of the dipole and θ the angle between r_2 and the dipole. It is obvious that the second term becomes negligible for the higher members of an electronic series, and thus they may be expected to conform to the Rydberg series. Further it can be shown that the values of the dipole moment usually associated with a CH_2 or CH_3 group can produce quite large effects on the ultraviolet absorption spectra and ionization potentials of polyatomic molecules. Thus the method used in getting these electronic series should be to try and fit the higher members into a Rydberg series and then to fit in the lower members by their intensities and the fact that they should fall fairly close to where the band of the Rydberg series would fall. Similarities in vibration pattern also help where these can be observed.

The extremely diffuse band at 1745A (57,310 cm^{-1}) can possibly be a lower member of Class I though it is very far off the series. If we assume the predissociation of this band to be due to

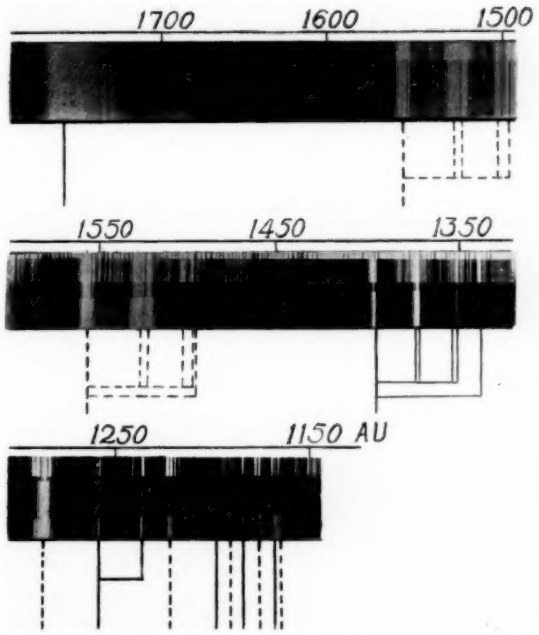

FIG. 1. The far ultraviolet absorption spectrum of formaldehyde.

interaction with the ground state the process being $H_2CO \rightarrow CH_2 + O$ we find the heat of dissociation of the C=O bond to be about 164 Cal./mole which is in fairly good agreement with the value ~172 Cal./mole obtained from thermochemical data. The author has also observed that all the bands in acetaldehyde and acetone which fall in the region below 1745A are predissociated, the strength of the predissociation depending on how far the bands are removed from this wavelength. The bands at wavelengths longer than this are sharp. It is thus indicated that the C=O bond is roughly of the same strength in all three substances.

The series (i) and (ii) in H_2CO have approximately the same limit which is 10.83 ± 0.01 volts. This compares favorably with the value 11.3 ± 0.5 volts determined by T. N. Jewitt[3] for the ionization potential of formaldehyde by the methods of electron impact.

It is fairly certain that the ionization is from the C=O bond. If it were from the CH bond the ionization potential would be expected to be considerably higher and the bands would prob-

[3] T. N. Jewitt, Phys. Rev. **46**, 616 (1934).

ably start at about the same wavelength as the corresponding ones in methane[4] (i.e., around 1300A). Investigations of the spectra of acetaldehyde and acetone[5] also indicate that in these molecules the excitation is from the C=O bond.

There are only two electronic transitions for which the vibrational pattern is at all well developed. These are the bands at 1556A and 1397A. There are two frequency differences accompanying each. In the case of the first band the differences are 1250 cm^{-1} and 1470 cm^{-1} and for the second band they are 1120 cm^{-1} and 1260 cm^{-1}. These vibration frequencies are presumably types which involve vibration in the C=O bond. Herzberg[6] has found a frequency of 1187 cm^{-1} in the near ultraviolet absorption of formaldehyde which he attributes to a vibration in this bond. A few frequency differences of $\sim$2900 cm^{-1} involving vibrations in the CH bond were observed in the bands reported here but they are very weak.

Although about 150 bands could be observed, the value of giving a complete table of their wavelengths is questionable because the latter, even under high dispersion, cannot be determined very accurately as the bands do not possess sharp edges. A few things however can be said about particular cases: The band at 64,270 cm^{-1} is really a diffuse doublet with a separation of 80 cm^{-1}, the frequencies of the components being 64,230 cm^{-1} and 64,310 cm^{-1}. That at 71,600 cm^{-1} is likewise composed of two bands separated by 50 cm^{-1}. Also all the upper bands of series (ii) have multiple heads which are possibly analogous to the rR, etc., branches reported by Dieke and Kistiakowsky[7] for the near ultraviolet bands.

The spectra of the alkyl derivatives of H_2S and H_2O are given in Fig. 2. They were taken on the smaller spectrograph. It is immediately evident that the spectra of the compounds containing sulphur are all shifted to the long wavelength region relative to those containing oxygen. This is in accord with the fact that the ionization

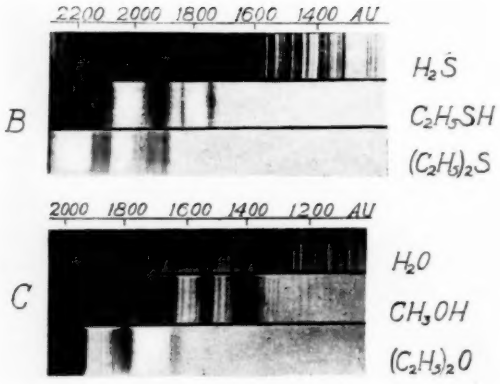

FIG. 2. The far ultraviolet absorption spectra of the alkyl derivatives of H_2S and H_2O.

potential of $S(1)$ is $\sim$10.3 volts and that of O(1) is $\sim$13.6 volts. The spectra of H_2S has been photographed under high dispersion. A complete discussion of it is reserved for publication elsewhere. The bands can be arranged into electronic series which go to several ionization potentials in the neighborhood of 10.5 volts. This agrees very well with the value 10.4 volts[8] obtained by electron impact.

The bands in H_2O have been followed to a limit around 980A by Rathenau.[9] Though no analysis has been made of the bands this limit is about 12.6 volts and it is obvious that they correspond to electronic series going to the ionization potential at 12.7 volts determined by Smyth and Mueller.[10] Thus it is fairly sure that the bands of the other molecules are of the same type, i.e., electronic series going to the first ionization potentials.

There is a very considerable amount of evidence available for spectra of the type reported here, which indicates that the bands of any particular alkyl compound start around the same wavelength and go to about the same ionization potential whatever the nature of the alkyl group, e.g., the spectrum of methyl not ethyl alcohol is given in Fig. 2. However, the spectrum of ethyl alcohol starts at almost the same wavelength. Further, the author has photographed the absorption spectra of ethyl, propyl,

[4] A. B. F. Duncan, J. Chem. Phys. **2**, 851 (1934).
[5] G. Scheibe, F. Povenz and C. F. Linstrom, Zeits. f. physik. Chemie **B20**, 292 (1933); W. A. Noyes, A. B. F. Duncan and W. M. Manning, J. Chem. Phys. **2**, 717 (1934).
[6] G. Herzberg, Trans. Faraday Soc. **27**, 378 (1931).
[7] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).
[8] C. A. MacKay, Phys. Rev. **24**, 319 (1924).
[9] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).
[10] H. D. Smyth and D. W. Mueller, Phys. Rev. **43**, 116 (1933).

isopropyl and butyl mercaptans and sulphides and found that they all begin around 2100A and 2300A, respectively. Also Scheibe, Herzberg[11] and others have obtained the spectra of methyl, ethyl and tertiary butyl iodide and found that they all start around 2010A. This must be related to the fact that the excitation is from the non-alkyl part of the molecule, and also that the dipole moments of the various alkyl groups are not sufficiently different to affect the term value of the excited electron.*

While it is still too early in the development of the spectra of polyatomic molecules to make many definite statements, some tentative remarks on these spectra may however be in order. The excitation in the case of the alcohols and the mercaptans is surely from the CO and the CS bonds, respectively, as the other bonds have higher ionization potentials. That of the sulphides and the ethers is also from the CO and CS bonds but the substitution of an alkyl group for a hydrogen atom has introduced a dipole which reduces the term values in the adjacent bonds (the negative end of the dipole is towards the excited electron). This diminishes the ionization potential and shifts the absorption bands towards the red. This successive shift towards the red is also found in the spectra of H_2CO, CH_3HCO and $(CH_3)_2CO$. Their estimated ionization potentials are 10.83, 10.5 and 10.1 volts, respectively.

It is possible to predict very roughly that for alcohols and ethers the first ionization potentials are around 10.8 and 10 volts, respectively, and for mercaptans and sulphides around 9 and 8.5 volts, respectively.

Preliminary measurements with fluorite spectrographs have been made on methyl and ethyl alcohol by Herzberg and Scheibe[11] and on methyl and ethyl ether by Scheibe and Grieneisen.[12] A wavelength table is not given here as it is intended in the near future to photograph the bands with higher dispersion and at a greater variety of pressures.

In conclusion the author wishes to express his gratitude to Dr. G. H. Dieke and Dr. K. F. Herzfeld for many discussions on the material of this article.

[11] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 390 (1930).

* A dipole of 0.3×10^{-18} e.s.u., such as is usually associated with a methyl group, will change the term value of an electron situated 1 Angstrom away by almost one electron volt and can thus change the position of the absorption bands by more than 100A.

[12] Scheibe and Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934).

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The Calculation of the Free Energy of Polyatomic Molecules from Spectroscopic Data. II

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The methods already developed for computing the free energy from spectroscopic data for diatomic molecules and for triatomic unsymmetrical rotators are extended to handle the case where one or more of the fundamental frequencies is degenerate. New tables, necessary for such calculations, have been computed and the procedure is illustrated by sample calculations for nitrous oxide, hydrogen cyanide and acetylene.

DURING recent years, the calculation of thermodynamic quantities from spectroscopic data has proved to be a most useful method of solving problems of chemical equilibrium. At the moment of writing, with the exception of steam,[1] carbon dioxide[2] and nitrous oxide,[2] precise calculations, taking account of the second and third order terms in the expression for the

[1] Gordon, J. Chem. Phys. **2**, 65 (1934).
[2] Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).

energy levels, have been carried out only for diatomic molecules;[3] consequently the extension of approximation methods to handle the more complicated polyatomic problem is clearly a matter of some importance. Steam (a typical example of a triatomic unsymmetrical rotator) is in some respects a specially simple case, since the question of vibrational degeneracy does not arise, and as a result the calculation can be brought under the diatomic form. For almost all other types of polyatomic molecules, however, one or more of the fundamental frequencies will be degenerate, and, as will be shown below, the rough assumption that the contribution of a doubly degenerate mode of vibration will be twice that of a singly degenerate mode of vibration with the same spectroscopic constants, may lead to appreciable errors in the calculated thermodynamic quantity. In the present paper, the methods previously developed for diatomic molecules[4] and for the triatomic unsymmetrical rotator[1] are extended to deal with the case where one (or more) of the frequencies is doubly degenerate; this extension has required the calculation of new tables which are appended.

The examples given below to illustrate the procedure are all for the collinear type of molecule, since it is only for these that a reasonably complete analysis of the energy levels has been made; the quantities tabulated in this paper, however, may be used in calculations for any type of molecule possessing a doubly degenerate mode of vibration. In the examples below, in order to illustrate the precision of the approximations, the calculation is sometimes carried to a greater number of significant figures than is justified by the accuracy of the experimental data.

The Triatomic Collinear Type, HCN and N_2O

The evaluation of the State Sum for this kind of molecule has recently been considered by Kassel,[2] who has computed the free energy, etc., of carbon dioxide and nitrous oxide by an extension of the methods he has previously used. Carbon dioxide is very much a special case owing to the resonance between two of the fundamentals, and since Kassel has dealt with it in detail, it will not be considered here. In general the vibrational levels for such molecules are given by an expression of the type

$$\epsilon_V/hc = v_1\omega_1+v_1^2x_{11}+v_2\omega_2+v_2^2x_{22}+l^2x_l + v_3\omega_3+v_3^2x_{33}+v_1v_2x_{12} + v_1v_3x_{13}+v_2v_3x_{23}. \quad (1)$$

Here v_1 and v_3 are the quantum numbers for the two nondegenerate "valence" frequencies ν_1 and ν_3, while v_2 is for the doubly degenerate "deformation" frequency ν_2. Such a degenerate frequency requires a subsidiary quantum number l to define it, l taking (for a given v_2) the v_2+1 values $-v_2, -v_2+2, \cdots, v_2-2, v_2$; v_1, v_2 and v_3 take all values from zero to their respective series limits.

The rotational levels are in general given by an expression of the ordinary diatomic form[5]

$$\epsilon_r/hc = B_vJ(J+1)+DJ^2(J+1)^2 \quad (2)$$

where $B_v=B_0(1-\alpha_1v_1-\alpha_2v_2-\alpha_3v_3+\cdots)$ and $J\geqq|l|$. When no question of symmetry nor of nuclear spin arises, the summation over J for moderate and high temperatures may be replaced without sensible error by an integration:[6]

$$\sum_{J\geqq|l|}(2J+1)\exp\left[-\{B_vJ(J+1)+DJ^2(J+1)^2\}hc/kT\right] \approx e^{-l^2/q_v}\cdot e^{1/4\,q_v}\cdot q_v(1+1/12q_v+d_v), \quad (3)$$

[3] For an excellent general survey of the present state of spectroscopic thermodynamics, see a recent series of review articles by Zeise, Zeits. f. Elektrochemie **39**, 758 (1933); **39**, 895 (1933); **40**, 662 (1934); **40**, 885 (1934).

[4] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).

[5] Neglecting the D term, the rotational energy is (strictly speaking) $Bhc(J^2+J-l^2)$; see Dennison, Rev. Mod. Phys. **3**, 280 (1931). For the purposes of computation, however, the term scheme can be represented most conveniently by Eqs. (1) and (2). See, for example, Choi and Barker, reference 12, pp. 780–783 and Adel and Barker, reference 11 p. 278. In order to represent the rotational energy accurately, it may be necessary to have terms involving powers of J other than those of Eq. (2); such terms will introduce in Eq. (3) items similar to those discussed in Gordon and Barnes' example 6, reference 4.

[6] The approximation of Eq. (3) decreases in percentage accuracy with increasing $|l|$ and decreasing q. For example, for $q=100$ and $D=0$, the values of (3) are

$\|l\|$	0	1	2	3	4
Direct summation	100.334	99.334	96.393	91.685	85.476
Eq. (3) (approx.)	100.334	99.336	96.400	91.698	85.499

For $q=500$ on the other hand, and $|l|=4$, the exact value is 484.52 while approximation (3) gives 484.58.

where $q_v = kT/B_v hc$, $d_v = -(2D/B_v)q_v$. As usual, for each atom possessing j_s units of nuclear spin, Eq. (3) must be multiplied through by a factor $(2j_s+1)$ if "absolute" thermodynamic quantities are desired.

In the rotational-vibrational state sum, the l-summation occurs as the factor

$$\sum_l \exp\left[-l^2(y_l+1/q_v)\right], \qquad (4)$$

where $y_l = x_l hc/kT$; this can be expanded and the resulting series in l^2, l^4, etc., can be summed as shown by Kassel.[2] The exponentials of the cross terms involving x_{12}, etc., can be expanded similarly, and by an obvious rearrangement the logarithm of the state sum can be written to a sufficiently good approximation

$$\ln Q_{RV} + E_0/RT \approx \sum_{i=1}^{3} (\ln Q_V + \epsilon_0/kT)_i + \ln q_0 + 1/4q_0 + \ln(1+f), \qquad (5)$$

where

$$\{e^{\epsilon_0/kT}\cdot Q_V\}_i = \{\sum p_v \cdot \exp\left[(\epsilon_0-\epsilon_V)/kT\right]\}_i = \{\sum p_v \cdot \exp\left[-vw+(v^2+v)wx\right]\}_i, \qquad (6)$$

$$f = 1/12q_0 + d_0 - (y_l+1/q_0)(\overline{v_2}^2+\overline{2v_2})/3 + (y_l+1/q_0)^2(3\overline{v_2}^4+12\overline{v_2}^3+8\overline{v_2}^2-8\overline{v_2})/30 + y_{12}\bar{v}_1\bar{v}_2 + y_{13}\bar{v}_1\bar{v}_3 + y_{23}\bar{v}_2\bar{v}_3 + \alpha_1\bar{v}_1 + \alpha_2\bar{v}_2 + \alpha_3\bar{v}_3, \qquad (7)$$

$$\overline{v_i^n} = \{\sum p_v \cdot v^n \cdot e^{-\epsilon_V/kT}\}_i / \{\sum p_v \cdot e^{-\epsilon_V/kT}\}_i, \qquad (8)$$

$$w = hc\omega/kT, \qquad (9)$$

$$p_v = 1 \quad \text{for} \quad i = 1, 3$$
$$= v+1 \quad \text{for} \quad i = 2, \qquad (10)$$

$$y_{ij} = -x_{ij}hc/kT. \qquad (11)$$

The replacement in f of q_v and d_v by q_0 and d_0 (the values of these quantities in the ground vibrational state) introduces only negligible errors in the final result. The neglect of some of the higher order term not included in Eq. (7) may be a more serious matter; such items, however, can be written out in any actual case where there is any doubt, e.g., terms such as $-y_{12}(y_l+1/q_0) \times (\bar{v}_1\overline{v_2}^3+2\bar{v}_1\overline{v_2}^2)/3$, $y_{12}^2\overline{v_1}^2\overline{v_2}^2/2$, $y_{12}y_{13}\overline{v_1}^2\bar{v}_2\bar{v}_3$, $\alpha_1 y_{23}\bar{v}_1\bar{v}_2\bar{v}_3$, $\alpha_1 y_{12}\overline{v_1}^2\bar{v}_2$ to mention only a few, and their values estimated. It will usually be found that such terms are relatively unimportant, and also that there is some mutual cancelation.

Of the quantities on the right of (5), $(\ln Q_V + \epsilon_0/kT)$, $\bar{v}$ and $\overline{v^2}$ can be found at once in the case of ν_1 and ν_3 from Gordon and Barnes' tables[4] for $w \geqq 0.6$ and $x \leqq 0.02$. For ν_2, the same three quantities for the same ranges of w and x may be obtained from Tables I, II and III of this paper. It should be noted that in entering the tables, the ω defining w is not the ω_i of Eq. (1) but is the difference $(\omega_i - x_{ii})$ of that equation, and that the x of the tables is the ratio $-x_{ii}/(\omega_i - x_{ii})$ of the equation (cf. Eq. (6) above). The only remaining untabulated quantities in Eq. (5) are $\overline{v_2^3}$ and $\overline{v_2^4}$ in the fourth term of Eq. (7). The contribution of this term is in general small and in most cases negligible; hence no serious error is introduced in estimating it by assuming that the vibrational levels of ν_2 are those of a harmonic oscillator with frequency $(\omega_2 + x_{22})$. On this assumption it is possible to write down closed expressions for $\overline{v_2^4}$, etc., and the term can be replaced by

$$(y_l+1/q_0)^2(t+13t^2+24t^3+12t^4), \qquad (12)$$

where $t = e^{-w}/(1-e^{-w})$.

Tables I, II and III were computed by summation (up to the series limit where necessary) for the first three entries in each column and then for every alternate entry in the column; the remaining numbers were obtained by interpolation, using the method of mean second differences. All entries were originally computed to an extra decimal place to ensure accuracy in the last place as printed. The intervals are sufficiently fine to permit interpolation using not more than second differences. For values of w and x outside the range of the tables, the integral approximations[7] discussed by Gordon and Barnes may be used in the case of ν_1 and ν_3; for ν_2, similar integral approximations can readily be set up. For example, the integral required to evaluate Q_V is in their notation $I_1 + I_4$; similarly, in the evaluation of

[7] There is an obvious misprint in their expression for I_2 at the bottom of p. 304. The equation should read

$$I_2 = (s^2+\tfrac{1}{2})\cdot I_1 - (1/2r)\cdot\{(s-Mr)\cdot[E_M] - (s-Nr)\cdot[E_N]\}.$$

TABLE I. $\ln Q_V + \epsilon_0/kT$ *as a function of* w *and* x *when* $p_v = v+1$.

w \ $x=$	0.0000	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200
0.60	1.5917	1.6130	1.6358	1.6604	1.6875	1.7182	1.7538	1.7953	1.8394
.62	1.5441	1.5645	1.5864	1.6099	1.6357	1.6647	1.6980	1.7368	1.7786
.64	1.4986	1.5182	1.5392	1.5616	1.5862	1.6136	1.6449	1.6813	1.7209
.66	1.4549	1.4738	1.4939	1.5155	1.5389	1.5648	1.5943	1.6285	1.6660
.68	1.4129	1.4312	1.4505	1.4712	1.4936	1.5182	1.5461	1.5782	1.6137
.70	1.3727	1.3903	1.4089	1.4287	1.4502	1.4737	1.5000	1.5303	1.5639
.72	1.3340	1.3510	1.3689	1.3880	1.4086	1.4310	1.4560	1.4845	1.5163
.74	1.2968	1.3132	1.3305	1.3489	1.3686	1.3900	1.4138	1.4408	1.4709
.76	1.2610	1.2768	1.2936	1.3113	1.3302	1.3507	1.3734	1.3989	1.4275
.78	1.2265	1.2418	1.2580	1.2751	1.2933	1.3130	1.3346	1.3588	1.3859
.80	1.1932	1.2081	1.2237	1.2402	1.2578	1.2767	1.2973	1.3204	1.3461
.82	1.1612	1.1756	1.1907	1.2066	1.2236	1.2418	1.2615	1.2835	1.3079
.84	1.1303	1.1442	1.1589	1.1743	1.1906	1.2081	1.2271	1.2480	1.2712
.86	1.1004	1.1139	1.1282	1.1431	1.1589	1.1757	1.1939	1.2139	1.2360
.88	1.0715	1.0847	1.0985	1.1129	1.1282	1.1444	1.1619	1.1811	1.2022
.90	1.0437	1.0564	1.0698	1.0838	1.0986	1.1142	1.1311	1.1495	1.1696
.92	1.0167	1.0291	1.0421	1.0557	1.0700	1.0851	1.1014	1.1190	1.1383
.94	0.9906	1.0027	1.0153	1.0285	1.0424	1.0570	1.0727	1.0896	1.1081
.96	.9654	0.9772	0.9894	1.0022	1.0156	1.0298	1.0449	1.0612	1.0790
0.98	.9410	.9524	.9643	0.9767	0.9898	1.0035	1.0181	1.0338	1.0509
1.00	0.9174	0.9285	0.9400	0.9521	0.9648	0.9781	0.9922	1.0073	1.0238

w \ $x=$	0.000	0.005	0.010	0.015	0.020	w \ $x=$	0.000	0.005	0.010	0.015	0.020
1.05	0.8614	0.8826	0.9056	0.9310	0.9598	2.1	0.2613	0.2685	0.2761	0.2841	0.2925
1.10	.8095	.8294	.8510	.8746	.9011	2.2	.2349	.2415	.2485	.2558	.2635
1.15	.7615	.7801	.8003	.8224	.8468	2.3	.2113	.2174	.2238	.2305	.2376
1.20	.7168	.7344	.7533	.7739	.7966	2.4	.1902	.1958	.2017	.2079	.2143
1.25	.6752	.6918	.7096	.7288	.7500	2.5	.1713	.1765	.1819	.1876	.1935
1.30	.6364	.6521	.6689	.6869	.7067	2.6	.1543	.1591	.1641	.1693	.1748
1.35	.6002	.6150	.6309	.6479	.6664	2.7	.1391	.1435	.1481	.1529	.1580
1.40	.5663	.5804	.5954	.6114	.6288	2.8	.1255	.1295	.1338	.1382	.1429
1.45	.5346	.5480	.5622	.5773	.5937	2.9	.1132	.1169	.1209	.1250	.1293
1.50	.5050	.5176	.5311	.5454	.5609	3.0	.1021	.1056	.1092	.1130	.1170
1.55	.4771	.4892	.5020	.5156	.5301	3.1	.0922	.0954	.0987	.1022	.1059
1.60	.4510	.4625	.4746	.4875	.5013	3.2	.0832	.0862	.0893	.0925	.0959
1.65	.4265	.4374	.4489	.4612	.4743	3.3	.0752	0779	.0807	.0837	.0869
1.70	.4035	.4139	.4248	.4365	.4489	3.4	.0679	.0704	.0730	.0758	.0787
1.75	.3818	.3917	.4022	.4133	.4250	3.5	.0613	.0637	.0661	.0687	.0713
1.80	.3614	.3708	.3808	.3914	.4026	3.6	.0554	.0576	.0598	.0622	.0646
1.85	.3421	.3512	.3607	.3708	.3814	3.7	.0501	.0521	.0541	.0563	.0586
1.90	.3240	.3327	.3418	.3513	.3615	3.8	.0453	.0471	.0490	.0510	.0531
1.95	.3069	.3152	.3239	.3330	.3427	3.9	.0409	.0426	.0444	.0462	.0482
2.00	0.2908	0.2987	0.3070	0.3158	0.3250	4.0	0.0370	0.0385	0.0402	0.0419	0.0437

$$\sum (v+1)\cdot v^n \cdot \exp\left[-vw+(v^2+v)wx\right],$$

where $n=1$ or 2, required in computing $\bar{v}_2$ and $\overline{v_2^2}$, the integrals involved are their I_4+I_7 and $(2s+r)I_7/r-I_5/r^2$, respectively.

The calculation of the entropy, heat content and heat capacity for molecules with a degenerate fundamental frequency would require additional tables similar to those constructed by Gordon and Barnes for the diatomic case, and the calculation of such tables is already under way. It should be noted in passing, however, that a table of F°/T as a function of temperature, accurate to 0.0005 cal./deg. will yield on tabular differentiation[8] values of the derivative (and consequently of S° and H/T) numerically accurate to 0.005 cal./deg., i.e., a value of the heat content even at 2000° reliable to 10 cal.; for most practical purposes, such accuracy is all that is required.

It is important to note that the principal difference between the method outlined here and that used by Kassel lies in the fact that he takes as a first approximation the vibrational energy levels to be those of a series of uncoupled harmonic oscillators, and in evaluating the state sum expands the exponentials of all anharmonic and cross terms as a correcting factor. In the present paper the first approximation consists in assuming that the vibrational levels are those of uncoupled anharmonic oscillators, and the exponential expansion applies only to the cross terms and the term involving x_l. The great advantage of Kassel's method lies in the fact that

[8] See any standard text on tabular methods, e.g., Rice, *Theory and Practice of Interpolation*, pp. 107–113 (1899).

TABLE II. $\bar{v}$ *as a function of* w *and* x *when* $p_v = v+1$.

w	x=0.0000	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200
0.60	2.433	2.513	2.604	2.711	2.845	3.026	3.265	3.570	3.848
.62	2.328	2.403	2.487	2.586	2.707	2.868	3.082	3.358	3.622
.64	2.231	2.300	2.379	2.470	2.580	2.724	2.915	3.165	3.414
.66	2.140	2.205	2.278	2.362	2.462	2.592	2.763	2.989	3.222
.68	2.054	2.115	2.183	2.261	2.353	2.470	2.624	2.828	3.045
.70	1.973	2.030	2.094	2.167	2.252	2.358	2.497	2.680	2.882
.72	1.897	1.951	2.010	2.078	2.157	2.254	2.380	2.545	2.731
.74	1.825	1.876	1.932	1.995	2.068	2.157	2.271	2.420	2.592
.76	1.757	1.805	1.858	1.917	1.985	2.067	2.170	2.306	2.464
.78	1.693	1.738	1.788	1.843	1.907	1.983	2.077	2.199	2.345
.80	1.632	1.675	1.722	1.774	1.833	1.903	1.990	2.101	2.235
.84	1.519	1.558	1.600	1.646	1.699	1.759	1.832	1.925	2.038
.88	1.418	1.452	1.490	1.531	1.578	1.631	1.694	1.772	1.868
.92	1.325	1.357	1.391	1.428	1.469	1.516	1.571	1.637	1.718
0.96	1.241	1.270	1.301	1.334	1.371	1.413	1.461	1.518	1.588
1.00	1.164	1.190	1.218	1.249	1.282	1.320	1.362	1.412	1.472

w	x=0.000	0.005	0.010	0.015	0.020
1.1	0.998	1.042	1.093	1.153	1.233
1.2	.862	0.898	0.939	0.987	1.047
1.3	.749	.779	.813	.852	0.899
1.4	.655	.680	.708	.741	.778
1.5	.574	.596	.620	.647	.678
1.6	.506	.525	.545	.568	.594
1.7	.447	.463	.481	.501	.522
1.8	.396	.410	.426	.443	.461
1.9	.352	.364	.378	.393	.409
2.0	.313	.324	.336	.349	.363
2.2	.249	.258	.267	.277	.288
2.4	.200	.207	.214	.222	.231
2.6	.160	.166	.172	.179	.186
2.8	.129	.134	.139	.145	.150
3.0	.105	.109	.113	.117	.122
3.2	.085	.088	.092	.095	.099
3.4	.069	.072	.075	.078	.081
3.6	.056	.058	.061	.064	.066
3.8	.046	.048	.050	.052	.054
4.0	0.037	0.039	0.041	0.043	0.044

TABLE III. $\overline{v^2}$ *as a function of* w *and* x *when* $p_v = v+1$.

w	x= 0.0000	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200
0.60	11.31	12.14	13.14	14.43	16.31	19.33	23.52	28.92	32.86
.62	10.46	11.20	12.10	13.23	14.83	17.37	20.98	25.76	29.54
.64	9.70	10.36	11.16	12.16	13.54	15.69	18.79	23.01	26.58
.66	9.01	9.60	10.32	11.20	12.40	14.23	16.89	20.61	23.94
.68	8.38	8.92	9.57	10.36	11.40	12.95	15.26	18.51	21.58
.70	7.81	8.30	8.89	9.59	10.51	11.84	13.84	16.68	19.49
.72	7.29	7.74	8.27	8.90	9.72	10.88	12.59	15.07	17.63
.74	6.82	7.23	7.70	8.28	9.01	10.01	11.49	13.66	15.99
.76	6.39	6.76	7.19	7.71	8.36	9.24	10.53	12.42	14.53
.78	5.99	6.33	6.72	7.20	7.78	8.56	9.68	11.32	13.22
.80	5.63	5.94	6.30	6.73	7.25	7.94	8.92	10.36	12.06
.84	4.98	5.25	5.55	5.91	6.33	6.88	7.64	8.74	10.10
.88	4.43	4.66	4.91	5.22	5.57	6.01	6.61	7.47	8.55
.92	3.96	4.15	4.37	4.63	4.93	5.29	5.76	6.43	7.30
0.96	3.55	3.71	3.90	4.12	4.38	4.69	5.06	5.59	6.29
1.00	3.20	3.34	3.51	3.69	3.91	4.16	4.47	4.90	5.46

w	x=0.000	0.005	0.010	0.015	0.020
1.1	2.49	2.71	2.99	3.37	3.96
1.2	1.98	2.14	2.34	2.60	2.98
1.3	1.59	1.71	1.86	2.05	2.30
1.4	1.30	1.39	1.50	1.64	1.82
1.5	1.07	1.14	1.23	1.33	1.46
1.6	0.89	0.95	1.02	1.10	1.20
1.7	.75	.79	0.85	0.91	0.99
1.8	.63	.67	.71	.76	.82
1.9	.54	.57	.60	.64	.69
2.0	.46	.49	.52	.55	.59
2.2	.34	.36	.38	.40	.43
2.4	.26	.27	.29	.30	.32
2.6	.20	.21	.22	.23	.24
2.8	.15	.16	.17	.18	.19
3.0	0.12	0.12	0.13	0.14	0.15

he is able to write closed expressions for all items and that as a result the use of tables is avoided; the disadvantage lies in the very complicated form of his correcting factor, the analog of the $(1+f)$ of Eq. (5) above (see, for example, his last equation on p. 1838 of reference 2).

There is one other difference of minor importance between the two methods. Kassel apparently takes all summations over a given vibrational quantum number to run from zero to infinity; in Gordon and Barnes' tables and in the tables of this paper, the summations run only from zero to the series limit. While it is very doubtful that in any actual case the use of summations to infinity will introduce any appreciable error in the calculated thermodynamic quantity, it is conceivable that with a combination of a large anharmonic term and high temperature it might be necessary to apply correcting terms to his expressions.

Example 1: N_2O at 1000°K

The vibrational energy[9] is given by $\epsilon_V/hc = 1288.7v_1 - 3.3v_1^2 + 593.0v_2 - 3.1v_2^2 + 2237.9v_3 - 13.8v_3^2 + 1.03l^2 - 9.8v_1v_2 - 26.7v_1v_3 - 13.3v_2v_3$. For ν_1, ν_2 and ν_3, w of the tables[10] is 1.8507, 0.85387 and 3.2254, respectively, and x is 0.00255, 0.00520 and 0.00613; hence from Table I of this paper and Gordon and Barnes' Tables I and II, $(\ln Q_V + \epsilon_0/kT)$ for ν_1, ν_2 and ν_3, is 0.1730, 1.1387 and 0.0423, respectively. Similarly, from Table II of this paper and Gordon and Barnes' Table V

[9] Plyler and Barker, Phys. Rev. **38**, 1827 (1931) as quoted by Kassel, reference 2. For revised values of the constants, see Barker, Phys. Rev. **41**, 369 (1932).

[10] In this and the other examples, the universal constants used were $h = 6.554\times10^{-27}$, $c = 2.9986\times10^{10}$, $k = 1.372\times10^{-16}$.

$\bar{v}$ is 0.201, 1.563 and 0.043, while from Table III of this paper, $\overline{v_2^2}$ is 8.35. The rotational-vibrational interaction terms and the second order rotational terms involving D, etc., are not known, but the moment of inertia is 66.1×10^{-40}. Hence the approximate value of $(\ln Q_{RV}+E_0/RT)$ from Eq. (5) is 8.7733, while the exact value found by summation over $v_1v_2v_3$ and l is 8.7731. In the calculation of f, the cross terms x_{12}, x_{13} and x_{23} contribute +0.00441, +0.00033 and +0.00128, respectively; the term $-(y_l+1/q_0)(\overline{v_2^2}+2\,\bar{v}_2)/3$ is −0.00579 and the fourth term in (7) is +0.00010, so that f is only +0.00038. The assumption that the levels could be treated as those of three harmonic oscillators (two singly degenerate with $\nu=1285$ and 2224 and one doubly degenerate with $\nu=590$) plus a rigid rotator with $I=66.1\times10^{-40}$ would have given the value $(\ln Q_{RV}+E_0/RT)=8.757$; the error here (0.016) comes almost entirely from the neglect of the anharmonic term in ν_2.

Example 2: HCN at 1500°K

The vibrational levels[11] are given by $2037.0\,v_1+52.0\,v_1^2+712.1\,v_2-2.9\,v_2^2+3364.2\,v_3-51.3\,v_3^2+3.1\,l^2-0.2\,v_1v_2-15.1\,v_1v_3-19.6\,v_2v_3$. The rotational constants[12] are $B_v=1.47890(1-0.00625\,v_1-0.00726\,v_3)$, $D=-3.63\times10^{-6}$; hence $q_0=708.08$, $d_0=0.00348$. The positive sign for the anharmonic term of ν_1 is a little surprising and leads to untabulated quantities; $(\ln Q_V+\epsilon_0/kT)$ and $\bar{v}$ for this fundamental, however, can be evaluated by the Kassel method[13] and are 0.1440 and 0.167, respectively. For ν_2 and ν_3, w is 0.68279 and 3.2616, and x is 0.00406 and 0.01502, respectively; hence, from the tables, for ν_2, $(\ln Q_V+\epsilon_0/kT)=1.4372$, $\bar{v}=2.144$ and $\overline{v^2}=9.22$. For ν_3 from Gordon and Barnes' tables $(\ln Q_V+\epsilon_0/kT)=0.0434$ and $\bar{v}=0.045$. Hence the approximate value of $(\ln Q_{RV}+E_0/RT)$ is 8.1758, as compared with the exact value obtained by summation, 8.1757. Here the terms x_{12}, x_{13} and x_{23} contribute +0.00007, +0.00011 and +0.00181 to f; $-(y_l+1/q_0)(\overline{v_2^2}+2\bar{v}_2)/3$ is −0.01967, $1/12q_0=0.00012$, α_1v_1 is +0.00104, $\alpha_3\bar{v}_3$ is +0.00033 and the fourth term in (7) is +0.00105; thus f is −0.01166. Here the harmonic oscillator-rigid rotator approximation would give $(\ln Q_{RV}+E_0/RT)=8.170$, with a resulting error of only 0.01 cal./deg. in $F°/T$; the reason for such close agreement in this case is that there is a fortuitous cancelation of the second and third order terms.

[11] Adel and Barker, Phys. Rev. **45**, 277 (1934).
[12] Badger and Binder, Phys. Rev. **37**, 800 (1931); Choi and Barker, Phys. Rev. **42**, 777 (1932); Herzberg and Spinks, Proc. Roy. Soc. **A147**, 434 (1934).
[13] Kassel, Phys. Rev. **43**, 364 (1933).

THE TETRA-ATOMIC COLLINEAR TYPE

Example 3: C_2H_2 at 1000°K

In spite of the very considerable amount of work that has been done on the acetylene spectrum, no entirely satisfactory analysis of the vibrational levels has been accomplished as yet. For the purpose of a numerical example illustrating the use of the method, however, either the Sutherland[14] or the Herzberg-Spinks[15] assignments may be used. Sutherland gives

$$\epsilon_V/hc=1974v_1+3421v_2-49.2v_2^2+3293v_3-5v_3^2+73Cv_4+605v_5-3v_1v_2-9v_1v_3-2v_1v_4-146.8v_2v_3-10v_2v_4+2v_2v_5-13v_3v_5-9v_4v_5.$$

Here ν_1, ν_2 and ν_3 are the three nondegenerate valence frequencies and ν_4 and ν_5 are the two doubly degenerate deformation frequencies. These latter are characterized by the subsidiary quantum numbers l_4 and l_5 which play the same role[16] as the l of Examples 1 and 2. Since the coefficients of l_4^2 and l_5^2 in the expression for ϵ_V are not known, the analog of Eq. (5) above becomes

$$\ln Q_{RV}+E_0/RT=\sum_{i=1}^{5}(\ln Q_V+\epsilon_0/kT)_i+1/4q_0+\ln q_0+\ln(1+f)-\ln 2, \quad (13)$$

where

$$f=y_{12}\bar{v}_1\bar{v}_2+\cdots+y_{45}\bar{v}_4\bar{v}_5+y_{12}\overline{v_1^2}\,\overline{v_2^2}/2+\cdots+y_{12}y_{13}\overline{v_1^2}\,\bar{v}_2\bar{v}_3+\cdots-(\overline{v_4^2}+2\bar{v}_4)/3q_0-(\overline{v_5^2}+2\bar{v}_5)/3q_0+\alpha_1\bar{v}_1+\cdots+\alpha_5\bar{v}_5+1/12q_0+d_0,$$

$(\ln Q_V+\epsilon_0/kT)$, $\bar{v}$, $\overline{v^2}$, q_0, y_{ij} and d_0 are as defined in Eqs. (6)–(11), p_v is 1 for $i=1$, 2 and 3, and is $v+1$ for $i=4$ or 5, and $-\ln 2$ is the symmetry correction. From Herzberg and Spinks' rotational

[14] Sutherland, Phys. Rev. **43**, 883 (1933).
[15] Herzberg and Spinks, Zeits. f. Physik **91**, 386 (1934).
[16] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

analysis $B_v = 1.17692(1-0.00524v_1-0.00550v_2-0.00521v_3-0.00051v_4+0.00263v_5)$, $D=-1.83\times10^{-6}$; hence $q_0=593.18$, and $d_0=0.00184$. The arguments for entering the tables and the corresponding tabulated quantities are

	ν_1	ν_2	ν_3	ν_4	ν_5
w	2.8276	4.9711	4.7241	1.04567	0.86661
x	0	0.0142	0.0015	0	0
$\ln Q_V+\epsilon_0/kT$	0.0610	0.0081	0.0090	0.8661	1.0907
$\bar{v}$	0.063	0.008	0.009	1.084	1.451
$\bar{v^2}$	..	..	..	2.85	4.60

Hence, from Eq. (15), $(\ln Q_{RV}+E_0/RT)=7.7416$, as compared with the exact value found by direct summation, 7.7412. The cross terms x_{12} to x_{35} make a relatively slight contribution (+0.00056) to f, but $y_{45}\bar{v}_4\bar{v}_5$ and $(y_{45})^2\cdot\overline{v_4^2v_5^2}/2$ are +0.02027 and +0.00109, respectively; the terms involving α altogether amount to −0.00288, while $-(\overline{v_4^2}+2\bar{v}_4)/3q_0$ and $-(\overline{v_5^2}+2\,v_5)/3\,q_0$ are −0.00282 and −0.00421. A calculation assuming a rigid rotator ($B=1.177$) plus five harmonic oscillators ($\nu=1974$, 3372, 3288, 730 and 605, the last two degenerate) gives $(\ln Q_{RV}+E_0/RT)=7.728$ with a resulting error in F°/T of 0.03 cal./deg.

Herzberg and Spinks[15] have recently given a different interpretation to the overtone and combination bands in the spectrum; their assignment is in some respects more satisfactory than Sutherland's (particularly as regards the valence overtones and combinations) but leads to surprisingly large values for the anharmonic term for ν_5 (-26.3 cm^{-1}) and for the cross term x_{45} (-18.8 cm^{-1}). If, however, Sutherland's assignment of the band at 2683 cm^{-1} as $\nu_3-\nu_5$ be retained (which involves taking the band at 2670 cm^{-1} as $\nu_1+\nu_4+\nu_5-\nu_5$) and the remainder of Herzberg and Spink's Table V be accepted unaltered, the expression for the vibrational energy becomes

$$\epsilon_V/hc = 1974v_1+3358.4v_2+13.6v_2^2+3318.4v_3-30.4v_3^2+729.3v_4+609.7v_5-4.7v_5^2-4.9v_1v_2-4.9v_1v_3-1.3v_1v_4-26.2v_1v_5-112.1v_2v_3-9.3v_2v_4-1.2v_2v_5+5.0v_3v_5-5.8v_4v_5.$$

This gives for ν_5, $w=614.4$ $hc/kT=0.88008$ and $x=4.7/614.4=0.00765$. The tabulated quantities are

	ν_1	ν_2	ν_3	ν_4	ν_5
$\ln Q_V+\epsilon_0/kT$	0.0610	0.0080	0.0090	0.8671	1.1137
$\bar{v}$	0.063	0.008	0.009	1.086	1.534
$\bar{v^2}$	0.07	0.01	0.01	2.85	5.24

With the same rotational constants as before, Eq. (13) gives $(\ln Q_{RV}+E_0/RT)=7.7615$, as compared with the exact value found by summation, 7.7613. The cross terms x_{ij} and their powers altogether contribute +0.01853 to f; of this terms of the type $y_{ij}\bar{v}_i\bar{v}_j$ amount to +0.01764; $(y_{45})^2\overline{v_4^2v_5^2}/2=+0.0052$, $(y_{15})^2\cdot\overline{v_1^2v_5^2}/2=0.00026$ and $y_{45}y_{15}\bar{v}_1\bar{v}_4\overline{v_5^2}=0.00011$. The rotational-vibrational interaction terms $\alpha_1\bar{v}_1\cdots\alpha_5\bar{v}_5$ amount to −0.00306, so that f is +0.00996.

In conclusion, it should be emphasized that for the five gases so far considered (H_2O, CO_2, N_2O, HCN, C_2H_2) the rigid rotator-harmonic oscillator approximation will yield values of $(F^\circ-E_0^\circ)/T$ even for temperatures as high as 1000–1500°K accurate to better than 0.1 cal./deg., and in four of the five cases to better than 0.05 cal./deg. This agreement is to some extent due to a partial cancelation of the terms neglected, and while one cannot assert that such cancelation will necessarily occur, one would expect it to be the rule rather than the exception. This assumption, if verified by future calculations for other molecules, should be a matter of some importance to those interested in problems of chemical equilibrium; it implies that a knowledge of the moment (or moments) of inertia and of the fundamental frequencies is sufficient to permit the calculation of equilibrium constants for the temperature range of greatest experimental interest to better than ±5 percent.

The Lifetime of Free Hydroxyl

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(1) The reasons for various failures to observe the absorption spectrum of free hydroxyl radicals are discussed. (2) The absorption spectrum of OH in the electric discharge through water vapor is observed with a spectrograph of high resolving power. After interrupting the discharge, the presence of OH is traced by its absorption spectrum over time intervals up to 1/8 sec. (3) With alternating half-periods of 60 cycle a.c. cut out by a switch, the *emission* of OH *vanishes* almost entirely with the current whereas the *absorption persists* rather uniformly. It is concluded that the persistence of the absorption spectrum is to be attributed to a *long life of OH radicals* rather than a *long life of O and H atoms* furnishing a fresh supply of *short life OH radicals*. (4) The rotational intensity distribution within the OH band at strong currents (being anomalous to a lesser extent than at faint currents) indicates the presence of free OH in the discharge. (5) For a comparison of the present result with previous estimates, leading to a much shorter life of free hydroxyl, the number per sec. of emission processes of the OH band is measured, assuming that each of these processes leads to the production of one free OH radical. (6) The process by which OH radicals are consumed is discussed.

I. Problem and Previous Work

THE fact has been emphasized by H. N. Russell,[1] investigating absorption spectra of stellar atmospheres, that in the *visible* and *near ultraviolet* absorption spectra are to be observed preferably of *unstable* molecules, for example, the free radicals OH, NH, CN, whereas most *stable* molecules, such as H_2, N_2, O_2, CO_2, H_2O, have absorption spectra in the *extreme ultraviolet*. The reason is that most stable molecules, but not the unstable ones, have electronic configurations similar to those of the rare gases; hence they have high values of excitation energy. This preferred observation of free radicals by absorption spectra contrasts with the methods of chemical analysis. Although they have been well developed for stable molecules, there is no direct chemical test for the simplest free radicals like OH or NH. These radicals, however, play a major hypothetical part in theories of chemical reactions. Here evidently is a chance for the spectroscopist to supplement the chemical analysis of gases, that is, to observe radicals during the progress of a reaction. Although the *absorption* spectra of most simple radicals have not been observed as yet, their wavelengths can be predicted since their *emission* spectra are known as well as the spectra of stable molecules.

The OH group and its reactions present a problem of major interest because of the part they play in the hydrogen oxygen reaction.[2] Furthermore, there is a particular interest in recent results of Rodebush and Wahl[3] who suggest a *bimolecular* association $OH+OH \rightarrow H_2O_2$ as the principal process by which the OH radicals are consumed.

In the present paper the life of OH radicals, produced by an electric discharge through H_2O vapor as they disappear by a chemical reaction after the interruption of the discharge, is being investigated. The concentration of OH is estimated by the intensity of the absorption spectrum.

Quantitative results regarding the concentration can be derived from absorption, not from emission spectra. The reason is that within certain limits, in particular at low pressures, the *absorption coefficient*—not the intensity of the absorption line measured against the background—is proportional to the concentration of the absorbing molecules (Beer's law)[4] whereas the intensity of the *emission spectrum* is very largely determined by other uncontrollable factors.[5]

[1] Lecture at the Harvard Observatory, 1931; Astrophys. J. **79**, 317 (1934).

[2] Cf. K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie*, p. 257.

[3] W. H. Rodebush and M. H. Wahl, J. Chem. Phys. **1**, 696 (1933); cf. G. I. Lavin and F. B. Stewart, Proc. Nat. Acad. Sci. **15**, 829 (1929).

[4] R. W. Wood, *Physical Optics*, 3d ed. p. 101; Macmillan Company (1934).

[5] The method of Bay and Steiner (Zeits. f. physik. Chemie **3**, 149 (1929)), based on the intensity of *emission* spectra, does not apply to the OH radical, since in the electric discharges the OH′ is largely generated directly from H_2O so that the intensity of the OH band fails to indicate the concentration of OH.

Hence by photometry the absorption spectrum gives evidence of the concentration of the absorbing gas, but—except after special calibration—only of *relative* values, since an unknown probability of transition goes in determining the *absolute* values. It is intended to calibrate the absorption spectra thus obtained with a known partial pressure of free OH radicals and so to proceed to the measurement of the *absolute* value of their concentration. This will be attempted by thermal dissociation of H_2O vapor according to Bonhoeffer and Reichardt.[6]

For rapid reactions the absorption spectra have to be taken in snapshots. In order to secure sufficient exposure, the chemical process and the snapshot have to be repeated periodically.

In recent years there have been reports of numerous attempts to observe the *absorption* spectrum of OH in *chemical reactions* or *electric discharges*.[7] These attempts, however, have failed,[8] although in the electric discharge through water vapor the *emission* spectrum, connected with the normal state of the OH molecule, appears very strongly; so strongly, as a matter of fact, that the emission of OH forms one of the most annoying spectral impurities. The *absorption* spectrum of OH has been observed, however, in *thermally dissociated* water vapor at temperatures up to 1600°C by Bonhoeffer and Reichardt.[9] The complete failure to observe the absorption spectrum of OH in chemical reactions or electric discharges led to the conclusion that, in any case, the concentration of OH is extremely small since the high reactivity limits the lives of these radicals to a very short period. Bonhoeffer and Reichardt were able to establish an upper limit for the concentration of OH present in the electric discharge through water vapor.

It seems probable that all failures to observe the absorption spectrum of OH in reactions or discharges have in common that the experiments have been undertaken with medium sized spectroscopic instruments. To observe faint and sharp absorption lines, however, is much more difficult than is the corresponding problem for emission. A faint, sharp *emission* line, when photographed with an instrument like a medium size quartz spectrograph, *appears broader* than it actually is emitted from the source. A faint, sharp *absorption* line, however, when photographed with the same instrument, *disappears* entirely, since its observation is about equivalent to the resolution of *two closely adjacent emission* lines.[10] For the most sensitive investigation of absorption spectra a spectrograph is required with a resolving power comparable with the width of the absorption lines to be observed. The great increase of sensitivity obtained by observing absorption lines with high resolving power becomes evident by the following comparison: While the quartz spectrograph fails to show any OH absorption spectrum in the electric discharge through H_2O vapor with the carbon arc furnishing the continuous background, the 21-foot grating reveals an undesirable OH absorption spectrum even without the discharge through H_2O in any carbon arc in air although operated in carefully dried air with purest carbons just baked out.

There is an essential difference between chemical processes in the discharge and other chemical processes in that the discharge produces excited and ionized states of all possible energy values, some of them much higher than the energies available in most chemical reactions. It can be assumed, however, that the *unstable* excited states of atoms and molecules radiate within so short a time interval that they are not to be observed after interrupting the discharge with the rotating disk method. *Ions and electrons* recombine very probably at such a high rate because of the Coulomb force of attraction that they may be just barely observable with the same method.[11] The recombination of *atoms and radicals* is probably by far the slowest process

[6] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928).

[7] H. C. Urey and G. I. Lavin, J. Am. Chem. Soc. **51**, 3293 (1929); K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie **14**, 1 (1931); W. Frankenburger and H. Klinkhardt, Zeits. f. physik. Chemie **15**, 440 (1932); P. Harteck, Trans. Faraday Soc. **30**, 139 (1934); K. H. Geib and P. Harteck, Zeits. f. physik. Chemie **A170**, 1 (1934).

[8] The absorption spectrum of OH, occasionally observed in the under water spark by H. Stücklen (Zeits. f. Physik **30**, 27 (1924)) is an exception.

[9] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928); cf. E. Hulthen and R. V. Zumstein, Phys. Rev. **28**, 14 (1926).

[10] Cf. W. H. J. Childs and R. Mecke, Zeits. f. Physik **68**, 353 (1931).

[11] C. Kenty, Phys. Rev. **32**, 624 (1928); L. J. Hayner, Zeits. f. Physik **35**, 365 (1925).

after interrupting the discharge. This chemical process is presumably the only one actually observed in the present experiment. There might be exceptional cases, however, in which this chemical process, following an electric discharge, would differ from the ordinary chemical processes if *metastable* states of a considerable lifetime are produced. Such states do exist in very pure helium and very pure mercury vapor. Since small traces of impurities, in particular hydrogen, are very efficient in destroying metastable levels, it is expected that the metastables do not play a part for any appreciable period after the interruption of the discharge through H_2O. Hence the results of the present method are directly comparable with the results of chemical methods for the investigation of the rate of chemical reactions in gases.

Since the rate of reaction is strongly affected by the temperature, it is of interest that the temperature—also a rapid change of temperature—can be observed, as well as the concentration from absorption spectra, by measuring the intensity distribution within one branch of a band.

The advantage of the method of absorption spectra over those of chemical analyses is its power to recognize free radicals and trace the progress of a fast reaction by snapshots.

II. Persistence of OH Absorption Spectrum

a. Apparatus

The apparatus consisted of an electric discharge through water vapor, the absorption spectrum of which is to be observed; a source for the continuous spectrum; a synchronous motor, operating the electric switch and the optical shutter; and the spectrograph (Fig. 1).

The discharge tube with large nickel electrodes and quartz windows, containing water vapor, afforded a column of 1.27 m length and 5 cm diameter for the absorption experiment. The electrodes, fastened in side tubes, had a distance of 10 cm from the main body of the tube which served as the absorption tube. Before the final experiments the glass walls were carefully freed of sputtered metal. "Conductivity water," distilled several times in high vacuum, was used.

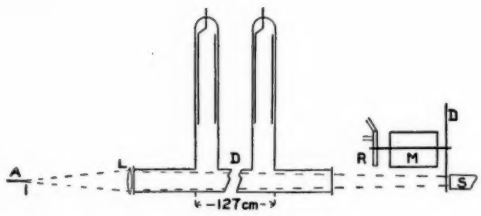

Fig. 1. Absorption experiment. *A*, carbon arc; *L*, quartz lens; *D*, discharge tubes; *M*, synchronous motor; *R*, revolving switch; *D*, sector disk; *S*, slit of spectrograph.

The source for the continuous spectrum offered an unexpectedly difficult problem. At 3100A the hydrogen discharge tube, emitting a perfectly uniform spectrum, gave an intensity, even with the highest current density obtainable, far inferior to the carbon arc. The carbon arc in air, however, was useless since it contributed a pronounced absorption spectrum of OH. By various experiments it was found that this absorption spectrum was due to the combustion in air of hydrogen compounds serving as binding material for the carbons. The carbon arc in flowing nitrogen, carefully dried, was applied. Its spectrum, however, was not quite continuous because of superimposed nitrogen bands, nor was its intensity quite uniform with time because of the irregular shaping of the carbon electrodes.

A synchronous motor carried on its axis a brass and Bakelite sector disk as a switch. It connected the discharge tube with the secondary of a transformer in most experiments for a half-period of 60 cycles a.c. and disconnected the tube for the next half-period or three half-periods. During this time interval the chemical recombination was investigated by the absorption spectrum. In order to determine the maximum time interval through which the absorption spectrum of OH could be traced, the speed of the revolving switch was reduced by gears to one-fifth of its former rate, the switch transmitting one full period of current and cutting out nine full periods.

An optical sector disk of Bakelite rotating on the same axis with the switch, immediately in front of the slit of the spectrograph, screened off the inevitable radiation emitted from the water vapor during the electric discharge running and let through only emission flashes of the continuous spectrum passing the water vapor within

short time intervals after interrupting the discharge. By varying the phase difference between electrical and optical sectors and observing the intensity of the absorption spectrum, decaying after the discharge, the lifetime of the OH molecules was investigated. With an optical sector of 12°, each individual flash lasted 1/900 sec.

A 21-foot Rowland concave grating served as a spectrograph. Its mounting had recently been rebuilt in a constant temperature room in the basement of the new Research Laboratory of Physics by Professor F. H. Crawford and Mr. D. W. Mann. Its second order at 3100A has a resolving power of 0.014A. On the other hand, the width of OH lines, when computed on the basis of the Doppler broadening at 400°C, is only 0.005A, considerably smaller than the resolving power. Hence an apparatus with higher resolving power would afford a still more sensitive spectroscopic test for OH radicals. In order to secure the highest resolving power a narrow slit and the fine grain Eastman IV−0 plates were used in spite of their very small speed.

Since an intermittent continuous spectrum was to be photographed with very high dispersion on slow photographic plates, a serious difficulty was expected from the lack of light intensity. Hence the experiment started from a systematic comparison of the various methods by which the intensity of illumination could be increased, in particular by compensating for the astigmatism. The results were published in a previous paper.[12] A cylindrical lens in front of the grating proved useful.[13] The times of exposure, including intermissions, were of the order of magnitude of 30 minutes.

b. Results

By using the apparatus described, the absorption spectrum of OH radicals came out clearly. (Fig. 2.) It was strongest when the water vapor pressure was high (2 mm) and the current strong. Because of the inevitable intense emission spectrum of the discharge, it was best observed immediately after the interruption of the current. It could be traced down to about 0.3 mm. At a pressure of 2 mm, by means of the slow interrupter, its decaying intensity could be followed after the interruption over the full period of 1/8 sec. Within this interval a considerable decay was observed (Fig. 3). The figure, however, does not express an average lifetime of OH radicals since it is largely dependent upon the sensitivity of the test. The time interval of 1/8 sec. holds for favorable conditions.

In order to compare the absorption spectra during the discharge and after the interruption, care must be taken that during the discharge the emission spectrum is faint as compared with the continuous background or else it would mask the absorption spectrum. Hence a small current (30 ma) through the water vapor and, in order to secure sufficient absorption, rather high pressure (2 mm) was applied. The intensity of absorption was not much stronger during the discharge running than after the interruption. Hardly any change was noticed within one half-period—in agreement with the total persistence of absorption observed as amounting to many half-periods of 60-cycle current.

The intensity distribution within the absorption band was very different from the one within the well-known OH emission band. The strong heads, characteristic in emission, disappeared in absorption. The reason is that in *absorption* the molecular rotation is low, mainly determined by the temperature, whereas in *emission* much higher rotational quanta come out with great intensity. The process exciting the abnormal rotation in emission has been discussed in a previous paper.[14]

Up to the present no quantitative photometric work, comparing concentrations of OH, could be carried through since the source of the continuous spectrum, the carbon arc in N_2, contributed traces of OH absorption spectra in a rather erratic way. It is easy to recognize the OH absorption due to the *discharge* which is unlike the one caused by the *arc* because of the widely different widths of the lines and intensity distributions of rotation. For photometric work, however, a perfectly uniform background is

[12] O. Oldenberg, J. Opt. Soc. Am. **22**, 441 (1932); cf. G. Dieke, J. Opt. Soc. Am. **23**, 274 (1933) and J. B. Green and R. A. Loring, J. Opt. Soc. Am. **24**, 348 (1934).

[13] W. J. Humphreys, Astrophys. J. **18**, 324 (1903); E. Gehrcke, Zeits. f. Instr. Kde. **31**, 217 (1911).

[14] O. Oldenberg, Phys. Rev. **46**, 210 (1934).

FIG. 2. Spectra of OH radicals (enlargement 9-fold); part of band 3064; (1) emission; (2) absorption.

FIG. 3. Decay of absorption spectrum after interruption of discharge; (1) 1/300 sec.; (2) 1/8 sec. after interruption.

indispensible. Therefore, only the estimate given above of the persistence of the OH absorption spectrum can be made as yet.

III. Nature of the Long Life Particles

As described in the preceding section, the absorption spectrum of OH radicals can be traced over a period as long as 1/8 sec. after the discharge is interrupted. This, however, does not necessarily indicate a correspondingly long life for the free OH radicals. Bonhoeffer and Pearson, discussing the afterglow, suggested an alternative; namely, that the long lives of the *O and H atoms* by slow recombination produce a fresh supply of OH radicals over a considerable period of time; these radicals are assumed to have a much shorter life. This is analogous to the persistence of the *molecular* emission spectrum in the well-known afterglow of nitrogen which is ascribed not to the long life of the molecules but to slowly recombining atoms.[15]

a. Lifetime not attributed to the recombination of O and H atoms

First, we shall compare the various possibilities of slow recombination of O and H atoms with the spectroscopic observations.

(*1*) *Triple collisions forming OH′*. Bonhoeffer and Pearson investigated various processes by which the band spectrum of OH might be excited. They proved by experiments that *in the discharge* the emission of OH is largely due to dissociation of H_2O and excitation of OH in one process (impact by fast electrons of 9 volts or more). This process has recently been confirmed by an independent argument.[16] The *afterglow* of the OH bands, however, discovered by Lavin and Stewart[17] must originate from another excitation process since outside of the discharge no fast electrons are present. Bonhoeffer and Pearson proved that H atoms in O_2 or O atoms in H_2 fail to excite the OH band but that H and O atoms when mixed produce the OH band with high intensity. They concluded that the afterglow is caused by $O+H\rightarrow OH'$, the energy of combination changing largely to excitation of OH; for known reasons triple collisions have to be assumed. Furthermore, they assumed a relatively short life of the OH radicals, estimated to 10^{-3} sec.

This theory, which well explains previous results, is to be correlated with the absorption spectra described. The underlying hypothesis (short life of OH, long lives of O and H forming a fresh supply of OH) leads us to predict that any change in the *supply formed per sec.* will be followed by a change in the *concentration* of OH within a time limited approximately by the life of OH($\sim$1/1000 sec.). Therefore a somewhat slower fluctuation of the supply ought to be accompanied by a corresponding fluctuation of the concentration. The cutting out of alternate half-periods of 60 cycle a.c. will cause a fluctuation of the discharge by which this theoretical prediction will be tested. By spectra taken in snapshots we can trace both the supply formed per sec. and the concentration. The *supply* is to be traced since all formation processes mentioned in the theory lead to *excited* OH radicals (during the discharge running by dissociation of H_2O into $OH'+H$ as the process of major probability

[15] G. Cario and J. Kaplan, Zeits. f. Physik **58**, 769 (1929).

[16] O. Oldenberg, Phys. Rev. **46**, 210 (1934).

[17] G. I. Lavin and F. B. Stewart, Proc. Nat. Acad. Sci. **15**, 829 (1929).

and as afterglow between discharges by O+H +M→OH′+M); hence each formation process of an OH radical is accompanied by an emission process of the OH band. Therefore, by measuring the intensity of the emission spectrum we actually register the supply formed per sec. of OH radicals. On the other hand, independently of any theory, by the absorption spectrum we can also observe the *concentration* of OH present. The theory under discussion predicts that the concentration of OH will fluctuate at the same rate as supply formed per sec. This becomes equivalent to the absorption spectrum of OH fluctuating at the same rate as the emission spectrum. This prediction is to be tested by snapshots of emission and absorption spectra during and between discharges.

With the same discharge through water vapor and the same sector disk and interrupter, letting through and cutting out alternate half-periods, and with a quartz spectrograph, the *emission* of OH was compared during and between discharges. It faded to an inferior order of magnitude after the interruption. For example, approximately the same photographic effect was produced *during* the discharge in 1/2 sec. and *between* discharges in 5 hours, the ratio being about 1 : 40,000. Therefore according to the theory under discussion—concentration rapidly changing with supply formed per second—we expect a striking decay of the concentration after the interruption. The absorption spectrum of OH, however, indicating the concentration, persisted during the intermission of one half-period without any striking decay as discussed above (II 2). This contradicts the theoretical prediction based on a very short life of OH, but long lives of O and H.

(2) *Triple collisions forming OH.* Secondly, we must consider O+H combining in triple collisions leading to OH instead of OH′. (In this case we cannot estimate the supply formed per sec. of OH from the intensity of emission.) There are two arguments against this process. Bonhoeffer and Pearson actually proved that two streams of gases, one containing H atoms, the other O atoms when flowing together, emit OH bands with high intensity. Hence the very small intensity of these bands, observed during the intermission, indicated that no large concentration of *both* atoms is present. Hence we fail to explain the absorption between discharges by the formation of OH from O and H. The other argument leading to the same conclusion is as follows: Granted that some OH radicals are supplied during and between discharges by recombination of O and H atoms, we still positively know that during the discharge another powerful source of OH radicals exists, the simultaneous dissociation of H_2O and excitation of OH by electron impact. Hence we should expect the concentration of OH to be considerably stronger *during* than *after* discharges—contrary to the observation. Therefore, the long lifetime of 1/8 sec. cannot be attributed to O and H atoms forming short life OH radicals. This argument applies against the catalytic effect of the wall as well as against triple collisions in the gas.

b. Lifetime attributed to OH radicals

Since the formation of OH from the atoms is excluded by the arguments just given, the plausible conclusion is that the persistence of the absorption spectrum of OH observed is due to a correspondingly long life of OH radicals.

Another argument against a very short lifetime of OH radicals is given by the fluorescence radiation of H_2O vapor, sensitized by Hg vapor. When excited by the Hg resonance line 2537 the OH band 3064 is strongly emitted.[18] The energy of 4.9 volt electrons, corresponding to the line 2537, is unable to dissociate the H_2O molecule and excite the OH radical in one process; hence we must assume two consecutive processes. It is most plausible to assume one impact of the second kind leading to dissociation of H_2O into OH+H and another to excitation of OH. The second process is probable only if an appreciable concentration of OH has been built up by the effect of the first process; or in other words, if the OH radicals have an appreciable lifetime.

c. Contribution of decomposing H_2O_2

In addition to the association of OH+OH, suggested by Rodebush and Wahl as the main reaction by which OH radicals *disappear*, one

[18] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1202 (1928). Under somewhat different conditions (a few mm H_2O vapor, sensitized fluorescence), Gaviola and Wood estimated the lifetime of free OH to the order of magnitude of 1/100 sec.

must consider the effect of another process *regenerating* these radicals. According to Geib H_2O_2 is decomposed by H atoms probably in the following process $H+H_2O_2 \rightarrow H_2O+OH$.[19] Is there a chance that the persistence of the absorption spectrum is caused by the slow liberation of OH radicals in this process from H_2O_2, while the radicals themselves have a much shorter life? Since so large a concentration of H_2O_2 was observed by Rodebush and Wahl among the gases pumped out of the discharge, it is hard to assume that a still much larger amount of H_2O_2 was originally produced which would give rise to the full amount of OH observed in the absorption spectrum. Moreover it is hard to assume that OH is stored up and bound in the shape of H_2O_2 from which it is gradually liberated only for very brief moments by H atoms, and yet the permanent concentration of *free* OH is so high, over a considerable period of time, that its absorption spectrum is well observable. It is probable, therefore, that the lifetime of OH observed in the absorption spectrum is largely determined by the real life of OH slowly recombining.

IV. Estimate of Concentration of OH from the Emission Spectrum

The absorption spectra described indicate only relative values of the concentration of OH under different conditions. They fail, however, to give evidence of the OH concentration as compared with the concentration of H_2O molecules. For the stationary concentration caused by a heavy current, the emission spectrum indicates an appreciable concentration of OH in the following experiment.

In a previous paper it was pointed out that the excitation process (*simultaneous* dissociation of H_2O and excitation of OH) leads to a characteristic *abnormal* rotation of the radiating OH, observed by the intensity distribution in the band spectrum. Conversely, we can recognize this excitation process from the strongly *abnormal* intensity distribution observed. On the other hand, free OH radicals in the discharge tube are certain to contribute a band of *normal* intensity distribution in emission since the absorption spectrum reveals normal rotation of the unexcited OH radicals present. (Section II b.) Therefore we may expect for a very small current (hardly any free OH present, hence all excited OH originating directly from H_2O) the greatest abnormal rotation and, on the other hand, for a very strong current a tendency towards normal rotation (smaller intensity of the very high rotational quanta) provided that an appreciable part of the intensity is due to free OH radicals present under the action of the current.

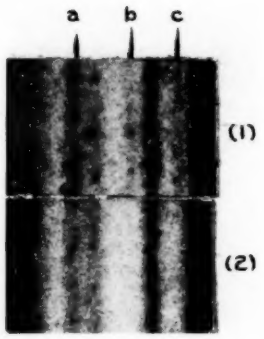

FIG. 4. Part of OH band (negative, quartz spectrograph, enlargement 55-fold). (1) weak current; (2) strong current. Abnormal rotation is pronounced at weak current; the following lines are enhanced; $a=R_1(17\frac{1}{2})$ and $R_2(15\frac{1}{2})$; $b=R_2(14\frac{1}{2})$; $c=R_2(13\frac{1}{2})$; rotational quantum number 3 or 4 would be most probable according to the temperature.

For a test the intensity distributions are compared for currents of 3 ma and 250 ma by spectra taken on the same plate, and with the same times of exposure in order to make them comparable, the intensity with the heavy current being reduced by dense gauze screens. Actually, as expected, heavy currents tend to reduce the high rotational lines. This effect can best be observed on lines of an R branch which have neighboring wavelengths although they belong to widely different rotational quanta (Fig. 4). This observation proves that for strong currents the partial pressure of OH radicals is appreciable. Since in the discharge the OH radical is preferred by its small energy of excitation (4.0 volts), a small concentration of free OH would be sufficient for the observed effect. In this argument the

[19] K. H. Geib, Zeits. f. physik. Chemie **A169**, 166 (1934). Mr. N. D. Smith called my attention to the possible effect of this reaction on the lifetime of OH. The next reaction, suggested by Geib, $OH+OH \rightarrow H_2O+O$ does not agree with the results of Rodebush and Wahl who proved the absence of atomic O from the discharge through H_2O vapor (cf. Section VIa). The alternative $OH+OH+M \rightarrow H_2O_2+M$ seems preferable. Since, however, this reaction regenerates half the H_2O_2, just decomposed, the yield of the first reaction would be higher than computed by Geib.

unknown contribution of H_2O_2 to the spectrum is neglected.

V. The Rate of Production of OH by the Process $H_2O+el \rightarrow OH'+H$

It might seem unsatisfactory to attribute the persistence of the OH absorption, observed as 1/8 sec., to the long life of OH radicals (Section IIIb) since all previous papers agree to a very short life of OH, estimated to 1/1000 sec. The reason for this discrepancy must be discussed.[20]

The main argument for a short life has been that the striking intensity of the emission band 3064 indicates a supply of OH formed per sec. so rich that its absorption spectrum could be expected to be observable with the quartz spectrograph (Section I).[21] It is difficult, however, to base this estimate of intensity upon a correct comparison. The observation shows only that the intensity of 3064 is strong when compared to other spectra.

The following comparison seems preferable: Assuming that each emission process of the band 3064 indicates the production of one OH radical and furthermore, assuming a lifetime as long as 1/8 sec. (Section IIb), the intensity of the emission band, measured in absolute units, leads to the *concentration* of OH (=number produced per sec.×lifetime) as far as it is produced by this observed process. This concentration is to be compared with a reasonable minimum concentration required for an absorption spectrum. The previous estimates (leading to a *short* life of OH) make us believe that this measurement of supply combined with a *long* lifetime of OH would lead to a concentration so high as to render the previous failures to observe the absorption spectrum inexplicable.

For this estimate the total number per sec. of emission processes of the band in the whole discharge must be measured. The densitometer trace of the band—with proper calibration of the photographic plate—yields a curve representing intensity in *arbitrary* units as a function of wavelengths. The emissive power of the surface of the discharge is obtained in *absolute* units from a quantitative comparison with the black body radiation at the same wavelength.[22] (In order to take the spectra of the discharge and the black body at 1415°K on the same plate with the same time of exposure, the intensity emitted from the discharge was reduced by the factor 950.) By integration over the whole surface of the discharge the total energy or number of quanta emitted per sec. from the whole discharge can be derived; that is, the total number of OH radicals generated per sec. by this observed process, the yield of which is to be estimated.

With a lifetime of 1/8 sec. a concentration of 4×10^{15} OH radicals per cm^3 results, or of 1 OH radical, as produced by the process considered, among 8000 H_2O molecules. (Apart from the uncertainty of the estimate caused in particular by the rather uncertain lifetime, it is easy to explain why the total concentration of OH must be considerably higher than the contribution of one process estimated here.) The result is that the intensity of the OH band observed in absolute units combined with a lifetime as long as 1/8 sec. does not lead to absurdly high values of the concentration of OH.

VI. Processes in the Discharge Through H_2O Vapor

a. Reactions consuming OH radicals

The reactions by which OH radicals disappear have been much discussed. It seems that the chemical processes are simpler in the electric discharge through water vapor than in the photochemical or thermal combination of H_2 and O_2. The reason is that in the discharge at moderate currents no free oxygen is formed. This is proved by the following three arguments: (1) Rodebush and Wahl proved by the Stern-Gerlach experiment that free O *atoms* are absent from the gases flowing out of the discharge. (2) They found no *molecular* oxygen in the discharge. (3) As re-

[20] The estimate of Bonhoeffer and Pearson, based on the idea that a considerable fraction of the total electric energy serves for producing OH', need not be discussed here since it leads only to a lower limit of the lifetime of OH.

[21] From the failure to observe the absorption spectrum Bonhoeffer and Pearson derived the concentration of OH as being less than 0.03 mm. It must be taken into account that the calibration of an absorption spectrum at four times the temperature and about five hundred times the pressure of the discharge cannot be quite accurate unless the spectrograph has very large resolving power, since in a medium size spectrograph a narrow line has a much larger tendency to escape from observation than a broad one.

[22] I am obliged to Dr. F. F. Rieke for the construction of the black body.

ported in Section III, the afterglow was exceedingly faint (in agreement with the results of Rodebush and Wahl and of Stoddart).[23] Its intensity, however, is known to be high if both O and H are present. Since there is no doubt about the presence of H, it follows that O is absent.[24] The conclusion agrees with the result of Stoddart who enhanced the afterglow by introducing O_2 to the H_2O vapor. Hence in the discharge through H_2O vapor with moderate current we are allowed to discard the consideration of O or O_2.

Among the gases pumped out of the discharge Rodebush and Wahl found a large concentration, about 50 percent, of H_2O_2. (Considering that H_2O_2 decomposes by the effect of the electric current as well as in the presence of H atoms, the concentration of H_2O_2 originally formed must have been still higher.) They explained previous failures to observe H_2O_2 by the catalytic effect of metal sputtered in the discharge tube, decomposing the H_2O_2. After a detailed discussion of all possible reactions leading to H_2O_2 they concluded that it is formed from OH+OH and that this is the main reaction by which OH disappears.

Harteck proved that the reaction by which OH disappears is homogeneous.[25] The rate of this reaction, however, seemed to bring in a difficulty. Rodebush and Wahl found the concentration of H_2O_2, pumped out of the discharge and condensed in a liquid air trap, to be independent of the time interval of the flow between discharge and trap, even for intervals as short as 1/300 sec. They inferred that the process $OH+OH \rightarrow H_2O_2$ is finished within a still shorter time. Considering this high rate of reaction, they discarded the idea of a triple collision and rather assumed a bimolecular association.[26] The argument for this rather unusual process becomes questionable, however, when considering the longer lifetime of OH reported in Section IIb. Instead, the following alternative, which was mentioned by Rodebush and Wahl themselves, seems preferable. It is assumed that the combination of $OH+OH \rightarrow H_2O_2$ goes on in the gas as well as within the liquid air trap so that for the measurement of the H_2O_2 concentration it does not matter whether a molecule is formed before or during condensation. Because of the reported much longer life of OH there is no argument left in favor of a *bimolecular* association. Consequently, the usual assumption of a *triple collision* for the process within the gas seems preferable. The experiments reported above are not sufficiently quantitative as yet to give direct evidence of the order of the reaction by which OH disappears.

More questionable than the homogeneous reactions discussed are the reactions of OH on the wall. Urey and Lavin[27] discovered the high reactivity of H_2O vapor when partly dissociated by an electric discharge. The present results agree with their assumption that OH radicals can be pumped out over considerable distances from the discharge. Yet it seems difficult to attribute the reactivity of the gas mixture to one or the other particle, for instance OH, formed in the discharge. According to Rodebush and Wahl it is true that in pure glass vessels only H, OH and H_2O_2 are produced by the discharge. But since H_2O_2 decomposes readily in the presence of a

[23] E. M. Stoddart, Phil. Mag. [7] **18**, 410 (1934).

[24] The absence of free oxygen might be interpreted by the assumption that in the electric discharge at moderate energies of electrons, OH radicals (as well as N_2 molecules) have a tendency to become excited or ionized rather than dissociated. This is to be expected from the high relative intensity of the 0–0 band emitted by the neutral molecule and the small change of internuclear distance that takes place by ionization. The values of these distances were kindly communicated to me by Professor F. W. Loomis; they are for the neutral molecule $r'=1.022$, $r''=0.979$ and for the ionized molecule $r'=1.139$ and $r''=1.027$. The absence of free oxygen is not easy to reconcile with the observation of G. von Elbe (J. Am. Chem. Soc. **55**, 62 (1933)), who found free oxygen in $H_2O_2+H_2$ when illuminated with the light of the zinc spark. It has been proved by Urey, Dawsey and Rice (J. Am. Chem. Soc. **51**, 1371 (1929)) that the intense zinc lines around 2100A excite the OH band in the fluorescence of H_2O_2. Hence OH is certainly produced. Nevertheless, the interpretation of the experiment is not unique since the continuous absorption spectrum of H_2O_2, observed between 2000 and 3100A is caused by the superposition of different processes; for instance light of 3100A, just coinciding with the band, clearly cannot produce dissociation of H_2O_2 and simultaneous excitation of OH which are produced by 2100A. The light of the zinc spark, therefore, is certain to produce other additional particles, making the interpretation rather uncertain.

[25] Cf. K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie **14**, 5 (1931).

[26] A triple collision is fundamentally required for the association of two *atoms* (like H+H); not, however, for the association of two *radicals* forming a fouratomic molecule (like $OH+OH \rightarrow H_2O_2$). A process of this type without a triple collision was reported by Farkas and Harteck (K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie*, p. 257). The probability was estimated on the basis of wave mechanics by N. Rosen (J. Chem. Phys. **1**, 319 (1933)).

[27] H. C. Urey and G. I. Lavin, J. Am. Chem. Soc. 51, 3290 (1929).

catalytic surface, oxygen also must be taken into consideration. There seems to be no chance to investigate individual effects of one or the other particle since Stoddart reports a failure to separate the hydroxyl from atomic hydrogen and oxygen.

b. Survey of processes in the discharge through H_2O vapor

There is no doubt about the principal primary process taking place in the discharge, the water molecule being broken up by electron impact: $H_2O+\text{electron}\rightarrow OH'+H$. (Instead of OH, the H atom might become excited; or both particles might be formed in their normal states.[28]) Since at moderate currents free atomic or molecular oxygen does not play a part, the processes to follow are the combinations of the particles mentioned, namely, $H+H+M\rightarrow H_2+M$ and $OH+OH+M\rightarrow H_2O_2+M$. The following competing associations must be considered: $H+OH+M\rightarrow H_2O+M$ obviously takes place but at a lower rate, or else the concentration of H_2O_2 could not be so high as actually observed in glass tubes with no metal present. For the same reason the reaction $OH+OH\rightarrow H_2O+O$ is supposed to have a lower rate; moreover, it would lead to atomic oxygen, the absence of which has been proved. The H_2O_2 formed in the discharge is partly broken up again by $H_2O_2+H\rightarrow H_2O+OH$. The reaction $OH+H_2\rightarrow H_2O+H$ is known to have an energy of activation $\geqq 14$ kcal. so that it does not take place at room temperature.[29]

A fundamental uncertainty is unavoidable in discussing processes in discharges. Excited atoms and molecules are being produced which, due to the high energy content of their *electronic structure*, might have a special reactivity, so high that even during the life of the excited state reactions are probable. Obviously the processes after the interruption of the discharge are easier to correlate to known chemical processes.

In the combination of H_2 and O_2, started by photochemically produced H atoms, H_2O_2 is formed, too. If the most recent theory is correct, in this photochemical experiment the H_2O_2 is formed over the intermediate compound HO_2 by association of H atoms with O_2 molecules.[30] It is of interest that in the electric discharge through H_2O vapor the formation of H_2O_2 takes place by an entirely different process.

The main results of the present paper are as follows: As a test for free OH radicals absorption spectra taken in snapshots were applied. They indicate in particular the change of concentration with time. The lifetime of free OH radicals is much longer than previously assumed, so long that no bimolecular association must be assumed for the process by which they disappear. Attempts will be made to obtain quantitative results by photographic photometry and to search for free OH radicals in other reactions.

The author wishes to express his sincere appreciation of the work done at the machine shop of this laboratory under the supervision of Mr. D. W. Mann, in particular by Mr. L. Cail, and of the glassblowing work of Mr. H. W. Leighton. He is greatly indebted to Professor G. B. Kistiakowsky and Dr. A. A. Frost for helpful discussions.

[28] J. Franck, H. Kuhn and G. Rollefson (Zeits. f. Physik **43**, 155 (1927)) describe analogous processes caused by absorption of light.

[29] W. Frankenburger and H. Klinkhardt, Zeits. f. physik. Chemie **15**, 436 (1932).

[30] K. H. Geib, Zeits. f. physik. Chemie **A169**, 161 (1934); K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie*, p. 262.

The Statistical Weights of the Rotational Levels of Polyatomic Molecules, Including Methane, Ammonia, Benzene, Cyclopropane and Ethylene

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A general method is described for calculating the statistical weights (degeneracies) of the energy levels of polyatomic molecules. Wave functions for a molecule are assumed to be expressible as linear combinations of products of the electronic, vibrational, rotational and nuclear spin functions. By using standard methods of group theory, the number of linear combinations of these products are found having the correct symmetry with respect to those permutations of identical atoms which are equivalent to rotations of the molecule. It is not necessary to find the combinations themselves. The molecules CH_4, CD_4, CH_3D, CHD_3, CH_2D_2, CH_3X, CD_3X, NH_3, ND_3, C_6H_6, C_3H_6 and C_2H_2 are treated. In addition noncombining species in polyatomic molecules and the splitting of energy levels due to the multiplicity of equilibrium configurations are discussed. Tables of statistical weights are given for the above molecules which could be used to interpret alternating intensities in rotation-vibration spectra or for more exact calculations of thermodynamic quantities than are usually made.

SEVERAL investigators[1] have calculated the quantum weights of the rotational states of a number of polyatomic molecules and the principles involved are well known. This paper indicates how such calculations can be considerably simplified (especially for complicated molecules) by the application of group theory. Methane is used as an illustration.

CONSTRUCTION OF APPROXIMATE WAVE FUNCTIONS

The wave function for a molecule is usually approximately expressed as a product of functions of the various coordinates; i.e.,

$$\psi = \psi_E \psi_V \psi_R \psi_T \psi_S, \qquad (1)$$

where the subscripts E, V, R, T and S indicate that the corresponding factor is a function of the electronic (including electron spin), vibrational, rotational, translational and nuclear spin coordinates. The electronic, vibrational and rotational wave functions depend on the choice of equilibrium configuration of the nuclei, regarded as distinguishable. Thus in defining the Eulerian angles θ, φ, and χ for $\psi_R(\theta, \varphi, \chi)$ it is necessary to define the moving Z' axis in terms of certain specified nuclei.

For this reason the wave function of Eq. (1) is not unique; there will exist a number of others, obtained from it by permuting identical nuclei. Some of these permutations may not, however, yield independent wave functions, since they may correspond to rotation of the molecule and therefore can be expressed in terms of other wave functions of the set in a manner which will be discussed later. Fig. 1 illustrates the two independent configurations for methane.

In addition to the degeneracy due to this cause, there may exist additional degeneracy due to the fact that ψ_R, ψ_S and sometimes ψ_V and ψ_E may themselves be degenerate. Thus for CH_4 ψ_S is 2^4 or 16-fold degenerate while ψ_S for CD_4 is 3^4 or 81-fold degenerate. Moreover, ψ_R for a spherical top (such as methane) has a degeneracy $(2J+1)^2$ for the energy level with quantum number J.

Although no one of the functions ψ of the type of Eq. (1) possesses such symmetry, the correct wave function for the molecule must be either completely symmetrical to interchange of members of a given set of identical particles or it must be completely antisymmetrical to such an interchange. Since protons obey Pauli's principle,

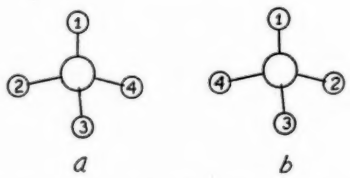

FIG. 1. The two different configurations or "frameworks" for methane.

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[1] F. Hund, Zeits. f. Physik **43**, 788 (1927); **43**, 805 (1927). These papers describe Hund's general method and treat NH_3; W. Elert, Zeits. f. Physik **51**, 6 (1928). This paper treats CH_4 by Hund's method which in this case is much more difficult than the group theory method; D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

CH_4 has antisymmetrical wave functions whereas CD_4 has symmetrical wave functions. In order to obtain a function with the proper symmetry character it is necessary to form linear combinations of the degenerate functions discussed above. The number of such combinations with the correct symmetry properties which can be formed is the quantum weight for that energy level.

In forming these combinations we first combine those functions for a given energy which correspond to the same configuration of the nuclei; i.e., the same "framework" of atoms, say *a* of Fig. 1. We form the combinations so that each one has the correct symmetry with respect to those permutations of identical particles which correspond to rotations of the molecule without change of framework. When we have done this for each framework, combinations involving functions based on different frameworks are made in such a manner that the resulting wave functions have the correct symmetry with respect to all possible permutations of identical nuclei.

In finding the number of combinations of functions based on one framework and possessing the correct symmetry properties, we use the methods of group theory.[2] The permutations of identical particles which are equivalent to rotations of the molecule form a group. The set of functions $\psi_E\psi_V\psi_R\psi_S$ based on one framework and belonging to one energy level constitute the basis of a reducible representation of this group which, by the construction of linear combinations, can be reduced so that the combinations divide into sets each of which forms an irreducible representation of the group. Only one certain irreducible representation will possess the required symmetry properties; we therefore seek the number of combinations of the functions $\psi_E\psi_V\psi_R\psi_S$ which correspond to this particular irreducible representation. (In methane this is the representation A of Table I, since all the rotations are equivalent to even permutations.) It is this number which is given by the formal methods of group theory without the need of actually constructing the combinations themselves.

TABLE I. *Irreducible representations of the group* **T**. $N=12$.

T	E	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E_1	1	1	ω	ω^2
E_2	1	1	ω^2	ω
T	3	-1	0	0

$\omega = e^{2\pi i/3}$

The work is further simplified by the fact that the symmetry of the set $\psi_E\psi_V\psi_R\psi_S$ can be obtained by finding the symmetry of ψ_E, ψ_V, ψ_R and ψ_S separately and then taking the "direct product" of their irreducible components. We shall therefore study each of these functions separately.

The electronic wave function ψ_E is ordinarily completely symmetrical for the normal state and the modifications in the method which are necessary in case this is not true will be obvious. The translational function ψ_T does not involve internal coordinates and is therefore symmetrical.

Symmetry of the Rotational Functions for Methane

The functions $\psi_R=\psi_{JKM}(\theta, \varphi, \chi)$ for methane are the solutions of the spherical top wave equation. The angles θ, φ and χ are the Eulerian angles, θ and φ being the ordinary polar coordinates of an arbitrarily chosen axis in the molecule. The group of permutations which correspond to rotations is in methane isomorphous with the symmetry point group **T**, which consists of those pure rotations which carry methane into itself. The irreducible representations of **T** have the characters[3] shown in Table I.

The symbols E, C_2, C_2 refer to the operations identity, twofold rotation, and threefold rotation, respectively. C_3' differs from C_3 in the sense of rotation. The symbols A, E_1, E_2 and T represent the irreducible representations. Applied to Fig. 1a, one C_2 is equivalent to the permutation (12)(34) while one C_3 is equivalent to (234), both of which are even permutations.

[2] See, for example, E. Wigner, *Gruppentheorie*, Vieweg and Sohn, 1931; B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik*, Springer, Berlin, 1932; A. Speiser, *Die Theorie der Gruppen von endlichen Ordnung*, Springer, Berlin, 1927; Also R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

[3] This table is taken from R. S. Mulliken, Phys. Rev. **43**, 279 (1933) which contains similar tables for all the crystallographic point groups; See also E. Wigner, Gött. Nachr., p. 133 (1930) and L. Tisza, Zeits. f. Physik **82**, 48 (1933).

TABLE II. *Characters for the representation of* **T** *formed by* ψ_R.

($p, k = 0, 1, 2, \cdots$. Multiply all characters by $2J+1$.)

	χ'_E	χ'_{C_2}	χ'_{C_3}	$\chi'_{C_3'}$
$J=6p+k$	$12p+2k+1$	$(-1)^k$	$(2/\sqrt{3})\sin\frac{2}{3}\pi(1-k)$	$(2/\sqrt{3})\sin\frac{2}{3}\pi(1-k)$

In order to reduce[3a] the representation formed by the functions $\psi_{JKM}(\theta, \varphi, \chi)$ for a given value of J it is necessary to know how these functions transform under the operations C_2 and C_3. If we choose the Z' axis in the molecule so that it coincides with one of the threefold axes, the operation C_3 will affect only the angle χ, changing it to $\chi \pm \frac{2}{3}\pi$. Since χ enters $\psi_{JKM}(\theta, \varphi, \chi)$ only by way of the factor[4] $e^{iK\chi}$, the transformation C_3 has the effect

$$\psi_{JKM}(\theta, \varphi, \chi) \xrightarrow{C_3} \psi_{JKM}(\theta, \varphi, \chi \pm \tfrac{2}{3}\pi) = e^{\pm(2\pi i/3)K}\psi_{JKM}(\theta, \varphi, \chi). \quad (2)$$

The character[5] χ'_{C_3} (which is the sum of the diagonal elements in the transformation matrix for C_3) is therefore[6]

$$(2J+1)\sum_{K=-J}^{J} e^{(2\pi i/3)K},$$

which has the values given in Table II.

With the choice of axis used above it is awkward to obtain χ'_{C_2}. However, we may make use of the fact that the choice of axis in a spherical top molecule is entirely arbitrary. Changing the axis is equivalent to a linear transformation of the functions $\psi_{JKM}(\theta, \varphi, \chi)$, with J and M fixed. Furthermore the diagonal sum of a matrix is invariant under such transformations. It is therefore convenient to calculate χ'_{C_2} with the axis coinciding with C_2, so that

$$\psi_{JKM}(\theta, \varphi, \chi) \xrightarrow{C_2} \psi_{JKM}(\theta, \varphi, \chi+\pi) = e^{K\pi i}\psi_{JKM}(\theta, \varphi, \chi), \quad (3)$$

which yields

$$\chi'_{C_2} = (2J+1)\sum_{K=-J}^{J}(-1)^K,$$

whose values are also given in Table II.

These characters and those in Table I are used in the standard group theory formula[7] to obtain the symmetries of the rotational functions ψ_R. These are given in Table III. (Since E and T are degenerate representations their coefficients in Table III need to be multiplied by 2 and 3, respectively, to give the number of linear combinations with these symmetries.)

TABLE III. *Symmetry of the rotational functions for methane.*

($p = 0, 1, 2, 3, \cdots$; $E = E_1 + E_2$)

$J=6p$	$(2J+1)$	$\{(p+1)A + \quad p \quad E + \quad 3p \quad T\}$
$J=6p+1$	$(2J+1)$	$\{\quad p \quad A + \quad p \quad E + (3p+1)T\}$
$J=6p+2$	$(2J+1)$	$\{\quad p \quad A + (p+1)E + (3p+1)T\}$
$J=6p+3$	$(2J+1)$	$\{(p+1)A + \quad p \quad E + (3p+2)T\}$
$J=6p+4$	$(2J+1)$	$\{(p+1)A + (p+1)E + (3p+2)T\}$
$J=6p+5$	$(2J+1)$	$\{\quad p \quad A + (p+1)E + (3p+3)T\}$

SYMMETRY OF VIBRATIONAL FUNCTIONS

A permutation of identical particles equivalent to a rotation of the molecule may affect ψ_V also. A simple illustration is shown in Fig. 2. Before interchange the distance (2–3) is greater than (1–3); after interchange these distances have exchanged magnitudes. But the normal coordinate for this motion is

$$Q = (2\text{–}3) - (1\text{–}3), \quad (4)$$

so that interchanging the magnitudes of these distances changes the sign of Q.

Since the wave function ψ_V is a function of the normal vibrations Q_k, the functions ψ_V may be transformed when the Q_k's are. In particular, the wave functions for a state with one quantum of one normal vibration excited transform in the same manner as the corresponding normal coordinates Q for that vibration.[7a] It is known[8]

[3a] The results of this paragraph may also be obtained from C. Eckart, Rev. Mod. Phys. **2**, 344 (1930) Eq. (111).

[4] Reiche and Rademaker, Zeits. f. Physik **39**, 444 (1926).

[5] See reference 2.

[6] The factor $(2J+1)$ comes from the $2J+1$ values of M associated with a given J.

[7] See reference 2.

[7a] The wave functions corresponding to overtone and combination levels usually have transformation properties different from those possessed by the normal coordinates, but obtainable from them. See Tisza, reference 3.

[8] For the application of group theory to molecular vibrations see E. Wigner, Gött. Nachr., p. 133 (1930); L.

FIG. 2. The effect of the permutation (12) on one of the normal coordinates of a linear triatomic molecule.

that the normal coordinates Q_k and the vibrational wave functions ψ_V have symmetry properties corresponding to the various irreducible representations of the symmetry point group for the molecule. This point group may contain reflections, inversions, etc., besides pure rotations. We are only interested in the pure rotations, but the effect of these on ψ_V may be easily obtained from a knowledge of the irreducible representation of the complete symmetry group to which ψ_V belongs.

Methane belongs to the point group[9] $\mathbf{T}_d$ (of which $\mathbf{T}$ is the rotational subgroup). Using the notation of Mulliken,[10] we can find[11] that there is one non-degenerate normal vibration (irreducible representation A_1 of $\mathbf{T}_d$), one doubly-degenerate vibration (E), and two triply-degenerate vibrations (T_2). The fundamental levels of ψ_V therefore have these symmetries. In this case it is very simple to find to what representations of $\mathbf{T}$ these various representations of $\mathbf{T}_d$ belong. One finds[10] that A_1 and A_2 of $\mathbf{T}_d$ belong to A of $\mathbf{T}$, E belongs to $E=E_1+E_2$, and T_1 and T_2 belong to T. Therefore, knowing[8] the symmetry of ψ_V with respect to $\mathbf{T}_d$, we can find its symmetry with respect to $\mathbf{T}$.

SYMMETRY OF THE NUCLEAR SPIN FUNCTIONS

The nuclear spin functions ψ_S form a basis of a representation of the group of permutations of identical atoms which are equivalent to rotations. For CH_4 there are 16 functions ψ_S, typical members of which are listed in Table IV, which gives the quantum number m_s for each atom. To obtain the characters for the representation formed by these functions, use is made of the fact that if a given permutation transforms one spin function into a different function that row of the transformation matrix has a zero diagonal element; if it transforms a function into itself, the diagonal element is unity. The character χ' for a given permutation is therefore equal to the number of spin functions unchanged by the given permutation. Thus the permutation (14)(23) (which is equivalent to a twofold rotation) leaves I and XVI invariant and also two functions from VI–XI; the character χ'_{C_2} is therefore 4. Similarly χ'_{C_3} is found to be 4 and evidently χ'_E is 16. Using these data and Table I we find that for CH_4

$$\psi_S=5A+E+3T. \tag{5}$$

TABLE IV. *Nuclear spin functions for CH_4.*

	1	2	3	4	No.
I	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	1
II–V	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$ etc.	4
VI–XI	$-\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$ etc.	6
XII–XV	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$ etc.	4
XVI	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1

For CD_4, $m_s=1$, 0, or -1 so that there are 81 functions ψ_S, of which typical members are given in Table V. From these the characters are found to be $\chi'_E=81$, $\chi'_{C_2}=9$, $\chi'_{C_3}=9$ so that for CD_4

$$\psi_S=15A+6E+18T. \tag{6}$$

TABLE V. *Nuclear spin functions for CD_4.*

1	2	3	4		No.	1	2	3	4		No.
1	1	1	1		1	−1	−1	−1	−1		1
0	1	1	1	etc.	4	−1	0	0	0	etc.	4
0	0	1	1	"	6	−1	−1	0	0	"	6
0	0	0	1	"	4	−1	−1	−1	0	"	4
0	0	0	0		1	1	1	−1	0	"	12
−1	1	1	1	"	4	0	0	1	−1	"	12
−1	−1	1	1	"	6	−1	−1	1	0	"	12
−1	−1	−1	1	"	4						

SYMMETRY OF $\psi_T\psi_E\psi_V\psi_R\psi_S$

The symmetry of the product of two functions is obtained by the use of the rule that the character χ' for the product of two independent functions is equal to the product of the characters for the two functions. In this way a multiplication table for the irreducible representations A, E, T can be built up. For $\mathbf{T}$ it is given in Table VI.

If a function x has the symmetry E_1, for example, while y has the symmetry T, the

Tisza, Zeits. f. Physik **82**, 48 (1933); E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

[9] $\mathbf{T}_d$ contains planes of symmetry, etc., in addition to the pure rotations of $\mathbf{T}$.

[10] R. S. Mulliken, reference 2.

[11] See, for example, E. B. Wilson, Jr., reference 8, Table III, 4.4a.

TABLE VI. *Multiplication table for irreducible representations of* **T**.

A	E_1	E_2	T
E_1	E_2	A	T
E_2	A	E_1	T
T	T	T	$A+E_1+E_2+2T$

product xy has the symmetry given under E_1 and opposite T in Table VI; namely, T.

By using the results of Table III, and Eqs. (5) or (6) in conjunction with Table VI, the symmetry of the functions $\psi_T\psi_E\psi_V\psi_R\psi_S$ can be obtained. It will be later shown that states involving nuclear spin functions of different permutation symmetries do not readily combine. It is therefore convenient to tabulate separately the states with different spin symmetry. The products $\psi_T\psi_E\psi_V\psi_R\psi_S$ must have the symmetry A in order to occur in nature. The number of linear combinations of these products (based on one framework) with the symmetry A and with the spin symmetry and vibration symmetry shown are listed in Table VII for CH_4 and in Table VIII for CD_4. It will be shown that these numbers are the statistical or quantum weights of the corresponding energy levels of the molecule.

CONSTRUCTION OF THE COMPLETE WAVE FUNCTIONS

The linear combinations enumerated in Tables VII and VIII are functions of all the coordinates, including spin, and have the correct symmetry properties with respect to those permutations of identical nuclei which correspond to rotations of the framework of nuclei upon which these functions are based. They do not have the correct symmetry with respect to other permutations of the identical atoms, since such permutations alter the framework. However, by adding (with the proper sign) the correct linear combination (call it ψ_A) for the framework A and the corresponding linear combination ψ_B for the framework B, a function can be constructed which has the correct symmetry properties with respect to any permutation of identical atoms. Thus the function

$$\Psi=\psi_A-\psi_B \tag{7}$$

will be completely antisymmetric for any interchange of protons; for example

$$(12)\Psi=\psi_B-\psi_A=-\Psi, \tag{8}$$

while

$$(123)\Psi=(123)\psi_A-(123)\psi_B$$
$$=\psi_A-\psi_B=\Psi, \text{ etc.} \tag{9}$$

Furthermore no new degeneracy is introduced by this step, because even when there are many independent frameworks for a molecule there will be only one combination of the functions based on the different frameworks with the correct symmetry.

To prove this, let us consider the representation of the entire permutation group (not the subgroup we have previously used) by the set of functions ψ_A, ψ_B, etc., one for each framework, the rotational properties of each being the

TABLE VII. *Weights of rotation-vibration levels for CH_4.* ($p=0, 1, 2, \cdots$. Multiply each weight by $2J+1$.)

$\psi_E\psi_V$	ψ_S	$J=6p$	$6p+1$	$6p+2$	$6p+3$	$6p+4$	$6p+5$
A	$5A$	$5(p+1)$	$5p$	$5p$	$5(p+1)$	$5(p+1)$	$5p$
	E	$2p$	$2p$	$2(p+1)$	$2p$	$2(p+1)$	$2(p+1)$
	$3T$	$9p$	$3(3p+1)$	$3(3p+1)$	$3(3p+2)$	$3(3p+2)$	$3(3p+3)$
	Total	$16p+5$	$16p+3$	$16p+5$	$16p+11$	$16p+13$	$16p+11$
E	$5A$	$10p$	$10p$	$10(p+1)$	$10p$	$10(p+1)$	$10(p+1)$
	E	$4p+2$	$4p$	$4p+2$	$4p+2$	$4p+4$	$4p+2$
	$3T$	$18p$	$18p+6$	$18p+6$	$18p+12$	$18p+12$	$18p+18$
	Total	$32p+2$	$32p+6$	$32p+18$	$32p+14$	$32p+26$	$32p+30$
T	$5A$	$15p$	$15p+5$	$15p+5$	$15p+10$	$15p+10$	$15p+15$
	E	$6p$	$6p+2$	$6p+2$	$6p+4$	$6p+4$	$6p+6$
	$3T$	$27p+3$	$27p+6$	$27p+12$	$27p+15$	$27p+21$	$27p+24$
	Total	$48p+3$	$48p+13$	$48p+19$	$48p+29$	$48p+35$	$48p+45$

TABLE VIII. *Weights of rotation-vibration levels for CD_4.*
($p=0, 1, 2, \cdots$. Multiply each weight by $2J+1$.)

$\psi_E\psi_V$	ψ_S	$J=6p$	$6p+1$	$6p+2$	$6p+3$	$6p+4$	$6p+5$
A	$15A$	$15p+15$	$15p$	$15p$	$15p+15$	$15p+15$	$15p$
	$6E$	$12p$	$12p$	$12p+12$	$12p$	$12p+12$	$12p+12$
	$18T$	$54p$	$54p+18$	$54p+18$	$54p+36$	$54p+36$	$54p+54$
	Total	$81p+15$	$81p+18$	$81p+30$	$81p+51$	$81p+63$	$81p+66$
E	$15A$	$30p$	$30p$	$30p+30$	$30p$	$30p+30$	$30p+30$
	$6E$	$24p+12$	$24p$	$24p+12$	$24p+12$	$24p+24$	$24p+12$
	$18T$	$108p$	$108p+36$	$108p+36$	$108p+72$	$108p+72$	$108p+108$
	Total	$162p+12$	$162p+36$	$162p+78$	$162p+84$	$162p+126$	$162p+150$
T	$15A$	$45p$	$45p+15$	$45p+15$	$45p+30$	$45p+30$	$45p+45$
	$6E$	$36p$	$36p+12$	$36p+12$	$36p+24$	$36p+24$	$36p+36$
	$18T$	$162p+18$	$162p+36$	$162p+72$	$162p+90$	$162p+126$	$162p+144$
	Total	$243p+18$	$243p+63$	$243p+99$	$243p+144$	$243p+180$	$243p+225$

same. There will be N/σ of these functions if N is the number of permutations in the group and σ the number of permutations equivalent to rotations (the symmetry number). Assume first that we seek symmetric Ψ's. For each ψ_A, etc., there will be σ permutations transforming ψ_A into itself. Each function will therefore contribute the quantity σ to $\Sigma(j)\chi'_j$ and since there are N/σ functions, $\Sigma(j)\chi'_j=N$. The number of linear combinations in the symmetrical irreducible representation is $n_1=(1/N)\Sigma(j)\chi'_j$ since every permutation has the character unity in this irreducible representation. We thus have $n_1=1$ as stated. For the antisymmetrical case, the same result is true, because whereas odd permutations have the character minus one in the antisymmetric irreducible representation, these same permutations will either change one function into another, contributing zero to the character, or they will transform ψ_A, etc., into $-\psi_A$ contributing -1 for each function so transformed. The minus signs cancel and we have the result as before that there is only one completely antisymmetric combination.

The numbers in Tables VII and VIII, which are the degeneracies of ψ_A or ψ_B are therefore the correct degeneracies or weights of Ψ.

As has been pointed out by other writers,[12] statistical mechanical calculations for high temperatures, at which many rotational levels are occupied, can be made with sufficient accuracy by disregarding the alternation in the weights of the various rotational states, assigning to each state the average weight obtained by dividing the total nuclear spin multiplicity (16 for CH_4, 81 for CD_4) by the classical symmetry number (here 12). That this is the correct average weight can be checked by the use of the numbers in Tables VII and VIII.

[12] Ludloff, Zeits. f. Physik **57**, 227 (1929); Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933); Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

NONCOMBINING SPECIES

Most types of perturbation which cause transitions do not involve the nuclear spin coordinates. Consequently, two states of a molecule with mutually orthogonal spin functions will be noncombining if only such perturbations occur. A well-known example is the case of the hydrogen molecule which may have either singlet or triplet spin functions and therefore exists in two noncombining forms (in the absence of catalysts). The deuterium molecule D_2, on the other hand, can have singlet, triplet, and quintet nuclear spin states, which presumably have long lifetimes. However, the singlet and quintet states have the same permutation symmetry and therefore are associated with the same set of rotational levels. Their equilibrium proportions will thus be the same at all attainable temperatures and there will be no way of changing their relative proportions.

A similar situation exists for polyatomic molecules. The spin functions can be divided according to their permutation symmetry and according to their multiplicity. States with spin functions differing either in symmetry or multiplicity will rarely combine unless a catalyst is present. However, as in D_2, the equilibrium proportions of certain sets of noncombining states will be unaffected by temperature so that for all practical purposes these sets of states constitute the noncombining states of interest. If two spin functions belong to the same irreducible representation of the group of permutations equivalent to rotations of the molecule (a subgroup of the

complete permutation group) the corresponding species will always exist in the same proportions and may be considered for practical purposes as one species. If they belong to different irreducible representations, they may have equilibrium proportions varying with the temperature. This is the justification for the statement previously made that there are three noncombining species in CH_4 and CD_4, having nuclear spin functions with symmetries A, E and T, respectively.

Symmetry of Rotational Functions for Symmetrical Top Molecules

In discussing other molecules it is necessary to know the transformation properties of symmetrical top functions. There are two types of rotations of interest. One is a rotation by an angle $2\pi j/n$ about the symmetry axis, where j and n are integers. Such a rotation changes the Eulerian angle χ into $\chi+2\pi j/n$ and therefore has the effect

$$\psi_R=\psi_{JKM}(\theta,\varphi,\chi)\overset{C_n^j}{\rightarrow}\psi_{JKM}(\theta,\varphi,\chi+2\pi j/n)$$
$$=e^{2\pi ijK/n}\psi_{JKM}(\theta,\varphi,\chi), \quad (10)$$

since the angle χ enters ψ_R only through the factor[4] $e^{iK\chi}$. Since there are only two functions for a given value of J and M and for a given energy; namely, ψ_{JKM} and ψ_{J-KM}, the character for such a rotation C is

$$\chi'_C=e^{2\pi ijK/n}+e^{-2\pi ijK/n}=2\cos(2\pi jK/n), \quad (11)$$

if $K\neq 0$, and unity if $K=0$. The other type of rotation is a twofold rotation about an axis perpendicular to the symmetry axis and making an angle α with the axis X' which is the origin of the angle χ measuring the rotation of the molecule about its symmetry axis. This rotation corresponds to changing θ into $\pi-\theta$, φ into $\pi+\varphi$ and as can be seen from Fig. 3, χ into $\pi-\chi+2\alpha$. Using the properties[4] of the symmetrical top functions we can find that

$$\psi_{JKM}(\pi-\theta,\pi+\varphi,\pi-\chi+2\alpha)$$
$$=(-1)^{J+\zeta+M}e^{iK(\pi+2\alpha)}\psi_{J-KM}(\theta,\varphi,\chi), \quad (12)$$

where ζ is the larger of $|K|$ and $|M|$. Therefore if $K\neq 0$, the character for this rotation is zero; if $K=0$, the character is $(-1)^J$.

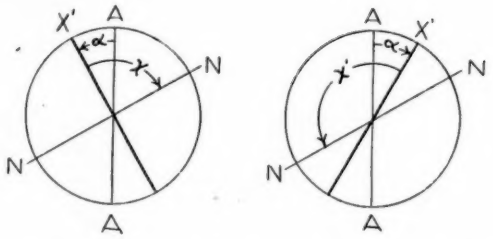

Fig. 3. The $X'Y'$ plane of a symmetrical top, showing the effect on the angle χ of a twofold rotation about an axis AA in the $X'Y'$ plane. NN is the nodal line. χ', the angle after the rotation, equals $\pi-\chi+2\alpha$.

Results for CH_3X, CD_3X, NH_3 and ND_3

These molecules belong to the rotational point group $\mathbf{C_3}$, which has the elements E, C_3 and C_3^2. Symmetrical top functions have the characters given in Table IX for these symmetry elements, obtained by using Eq. (11). Using these and the characters[13] $\chi_j^{(i)}$ for $\mathbf{C_3}$ we find that the rotational functions have the symmetries shown in Table X.

The spin functions for CH_3X (if X has no spin) are given in Table XI. From this it is seen that $\chi'_E=8$, $\chi'_{C_3}=2$, $\chi'_{C_3^2}=2$, so that ψ_S has the symmetry $4A+2E$. Combination of this result with the data of Table X yields Table XII

Table IX. *Characters for the representation of* $\mathbf{C_3}$ *formed by* ψ_R.
($p=0, 1, 2, \cdots$. Multiply all characters by $2J+1$.)

	χ'_E	χ'_{C_3}	$\chi'_{C_3^2}$
$K=0$	1	1	1
$\|K\|=3p$	2	2	2
$\|K\|=3p\pm1$	2	−1	−1

Table X. *Symmetry of the rotational functions for a molecule with rotational symmetry* $\mathbf{C_3}$.
($p=0, 1, 2, \cdots$.)

$K=0$	$(2J+1)A$
$\|K\|=3p$	$2(2J+1)A$
$\|K\|=3p\pm1$	$(2J+1)E$

Table XI. *Nuclear spin functions for* CH_3X.

1	2	3	No.
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3
$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	3
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	1

[13] See Mulliken, reference 2, for values of $\chi_j^{(i)}$ for C_3.

TABLE XII. *Weights of the vibration-rotation levels of CH_3X.* ($p=0, 1, 2, \cdots$. Multiply all weights by $2J+1$. No spin on X.)

$\psi_E\psi_V$: / ψ_S:	A			E		
	$4A$	$2E$	Total	$4A$	$2E$	Total
$K=0$	4	0	4	0	4	4
$\|K\|=3p$	8	0	8	0	8	8
$\|K\|=3p\pm1$	0	4	4	8	4	12

when the multiplication properties of $\mathbf{C}_3$ are used, which are: $A\times A=A$, $A\times E=E$, $E\times E=2A+E$. The complete wave function must have the symmetry A.

If X has a spin s, these weights must be multiplied by $2s+1$. Thus if X is D, a deuterium nucleus, $2s+1$ has the value 3. Table XII also can be used for NH_3, if all weights are multiplied by three, since nitrogen has a unit nuclear spin.

A similar treatment for CD_3X shows that if X has no spin ψ_S has the symmetry $11A+8E$, from which the weights in Table XIII may be deduced. If X has a spin s, these weights must be multiplied by $2s+1$, so that the factor for CD_3H is 2. By multiplying all weights by 3, Table XIII can also be used for ND_3.

TABLE XIII. *Weights for the vibration-rotation levels of CD_3X.* ($p=0, 1, 2, \cdots$. Multiply all weights by $2J+1$. X has no spin.)

$\psi_E\psi_V$: / ψ_S:	A			E		
	$11A$	$8E$	Total	$11A$	$8E$	Total
$K=0$	11	0	11	0	16	16
$\|K\|=3p$	22	0	22	0	32	32
$\|K\|=3p\pm1$	0	16	16	22	16	38

THE SPLITTING OF ENERGY LEVELS

In certain cases the energy levels which we have previously considered as degenerate are really split into two or more experimentally separable components. A well-known example is NH_3 in which the energy levels are nearly all doublets.[14] This splitting is due to the fact that the nitrogen atom can pass through the plane of the three hydrogen atoms without great difficulty so that it has two equivalent positions of minimum potential energy. Such an inversion corresponds to an interchange of identical hydrogen atoms (which changes the sign of Ψ), followed by a rotation of the molecule, which may or may not again change the sign of Ψ, depending on the nature of the functions ψ_R. The rotation required is equivalent to the transformation $\theta\rightarrow\pi-\theta$, $\varphi\rightarrow\pi+\varphi$, $\chi\rightarrow\pi-\chi$, which has the following effect on the symmetric top function ψ_{JKM}:

$$\psi_{JKM}(\theta, \varphi, \chi)\rightarrow\psi_{JKM}(\pi-\theta, \pi+\varphi, \pi-\chi)$$
$$=(-1)^{J+\zeta+K+M}\psi_{J-KM}(\theta, \varphi, \chi),$$

where ζ is the larger of $|K|$ and $|M|$. From this one finds that the levels with $K=0$ are not split but have total wave functions Ψ which are antisymmetric with respect to inversion when J is even and symmetric when J is odd. When $K\neq0$, the energy level is split into two components to each of which corresponds an equal number of wave functions, one component having functions which are symmetric towards inversion, the other component having antisymmetric functions.

The criterion as to whether or not the splitting is appreciable is the magnitude of the potential hill separating the two forms. Methane also possesses two forms but to pass from one to the other would require passing through too great a potential barrier so that no doubling is observed.

Since the electric moment changes sign on inversion, transitions in absorption occur only between states of opposite symmetry character with respect to inversion, whereas Raman transitions occur between states of like symmetry.

WEIGHTS FOR BENZENE

If benzene is a regular plane hexagon it has the point group symmetry $\mathbf{D}_{6h}$, the rotational subgroup for which is $\mathbf{D}_6$, with the elements E, C_2, $2C_3$, $2C_6$, $3C_2'$, $3C_2''$. Benzene is a symmetrical top, and so by using Eqs. (11) and (12) we can obtain the characters χ' shown in Table XIV for the representation of $\mathbf{D}_6$ formed by ψ_R. Using the character table for $\mathbf{D}_6$ given by Mulliken[2] and the values in Table XIV, we obtain the symmetries of the linear combinations of ψ_R given in Table XV.

The 2^6 nuclear spin functions for C_6H_6 are easily shown by the methods employed for the other molecules to combine to functions with the

[14] Dennison and Hardy, Phys. Rev. **39**, 938 (1932).

TABLE XIV. *Characters for the representation of* $\mathbf{D}_6$ *formed by* ψ_R. (p, k=0, 1, 2, 3, ···. Multiply all characters by $2J+1$.)

	χ'_E	χ'_{C_2}	χ'_{C_3}	χ'_{C_6}	$\chi'_{C_{2'}}$	$\chi'_{C_{2''}}$
$K=0$	1	1	1	1	$(-1)^J$	$(-1)^J$
$K=6p+k$	2	$2(-1)^k$	$2\cos 2\pi k/3$	$(-1)^k 2\cos 2\pi k/3$	0	0

symmetries $13A_1+A_2+7B_1+3B_2+11E^*+9E_*^*$. The total wave function for the molecule must fall in class B_1 since this represents complete antisymmetry.

TABLE XV. *Symmetry of the rotational functions for a molecule with rotational symmetry* $\mathbf{D}_6$.

(p=0, 1, 2, 3, ···.)

$K=0$, J even:	$(2J+1)A_1$
$K=0$, J odd:	$(2J+1)A_2$
$K=6p$:	$(2J+1)(A_1+A_2)$
$K=6p\pm1$:	$(2J+1)E_*^*$
$K=6p\pm2$:	$(2J+1)E^*$
$K=6p\pm3$:	$(2J+1)(B_1+B_2)$

The multiplication properties of the representations of $\mathbf{D}_6$ are

$A_2\times A_2=A_1$, $A_2\times B_i=B_j$, $A_2\times E^*=E^*$, $A_2\times E_*^*=E_*^*$, $B_i\times B_i=A_1$, $B_1\times B_2=A_2$, $B_i\times E^*=E_*^*$, $B_i\times E_*^*=E^*$, $E^*\times E^*=E_*^*\times E_*^*=A_1+A_2+E^*$, $E^*\times E_*^*=B_1+B_2+E_*^*$; where $i=1, 2$, $j=2, 1$.

With the use of these we can find the symmetry of $\psi_E\psi_V\psi_R\psi_S$ and from that the number of combinations with the total symmetry B_1; i.e., the quantum weights. These are given in Table XVI. Only the total weights are given.

TABLE XVI. *Weights of the vibration-rotation levels of* C_6H_6. (p=0, 1, 2, 3, ···. Multiply all weights by $2J+1$.)

$\psi_E\psi_V$:	A_1	A_2	B_1	B_2	E^*	E_*^*
$K=0$, J even	7	3	13	1	9	11
$K=0$, J odd	3	7	1	13	9	11
$K=6p$	10	10	14	14	18	22
$K=6p\pm1$	11	11	9	9	25	19
$K=6p\pm2$	9	9	11	11	19	25
$K=6p\pm3$	14	14	10	10	22	18

CYCLOPROPANE

The most reasonable model for C_3H_6, cyclopropane, has the point group symmetry $\mathbf{D}_{3h}$, for which the rotational subgroup is $\mathbf{D}_3$. Since the work of finding the weights for this molecule follows exactly the method previously used, only the results will be listed. These are given in Table XVII.

TABLE XVII. *Weights of the vibration-rotation levels of* C_3H_6. (p=0, 1, 2, 3, ···. Multiply all weights by $2J+1$.)

$\psi_E\psi_V$:	A_1	A_2	E
$K=0$, J even	8	16	20
$K=0$, J odd	16	8	20
$K=3p$	24	24	40
$K=3p\pm1$	20	20	44

ETHYLENE—AN ASYMMETRIC TOP

Ethylene[15] will serve as an illustration of how this method is to be used for asymmetric top molecules. The rotational functions for the asymmetrical top are of four kinds, differing in their symmetry with respect to the twofold rotations about the three principal axes of the molecule. Table XVIII gives the symmetries of these four kinds, which are labeled by the notation ++, +−, etc., introduced by Dennison.[16]

TABLE XVIII. *Characters for the representation of* $\mathbf{V}$ *formed by the four kinds of asymmetric top functions.*

	χ'_E	$\chi'_{C_2(z')}$	$\chi'_{C_2(y')}$	$\chi'_{C_2(x')}$	Irred. Rep.
++	1	1	1	1	A_1
+−	1	1	−1	−1	B_1
−−	1	−1	1	−1	B_2
−+	1	−1	−1	1	B_3

The spin functions for C_2H_4 are 16 in number and have the symmetry $7A_1+3B_1+3B_2+3B_3$, as can be verified by using the methods previously described. The multiplication table for $\mathbf{V}$ is: $A_1\times A_1=A_1$, $A_1\times B_i=B_i$, $B_i\times B_i=A_1$, $B_1\times B_2=B_3$, $B_1\times B_3=B_2$, $B_2\times B_3=B_1$. The symmetry of $\psi_E\psi_V\psi_R\psi_S$ can be found by the use of this information and the number of combinations with the symmetry A_1 (which corresponds to antisymmetric or symmetric wave functions)

[15] These weights have been previously calculated by Professor R. M. Badger but have not been published.

[16] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

TABLE XIX. *Weights for the vibration-rotation levels of C_2H_4.* (Multiply all weights by $2J+1$.)

$\psi_E\psi_V$:	A_1	B_1	B_2	B_3
$++$	7	3	3	3
$+-$	3	7	3	3
$--$	3	3	7	3
$-+$	3	3	3	7

TABLE XX. *Weights for the vibration-rotation levels of CH_2D_2.* (Multiply all weights by $2J+1$.)

$\psi_E\psi_V$:	A	B
sym. (K even)	15	21
antisym. (K odd)	21	15

obtained. These are the weights given in Table XIX.

The molecule CH_2D_2 (methane) is also an asymmetric top with the rotational symmetry C_2. There will be only two symmetry classes of rotational levels (with respect to C_2), those symmetrical to the twofold axis and those antisymmetrical. The vibrational and spin functions can likewise be divided into these two classes. The weights obtained are given in Table XX.

In conclusion I should like to express my appreciation to Professor J. H. Van Vleck for suggesting this problem and for valuable criticism in connection with it.

MAY, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

Dielectric Constant Studies

V. Anomalous Dispersion of Lecithin in Viscous Mineral Oils

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(Received January 14, 1935)

A unique receiver and accompanying cell for determining dielectric constants by the resonance method were constructed. Their design is such as to reduce to a minimum several types of error inherent in the resonance method. Dielectric constant measurements were made on five solutions of lecithin in very viscous mineral oils at three temperatures and at six wavelengths. Three distinct methods were employed: (1) refractometer method—frequency of D line of sodium, (2) resonance method—32.8 m, 94 m, 320 m, 1308 m, (3) bridge method—precision Wheatstone bridge, 1036 cycles. Analyses of the experimental curves and comparisons with theoretical Debye curves definitely indicate dispersion though not of a simple type. Another series of measurements made on one solution at 16 different wavelengths covering the range from 40 m to 5,000,000 m still failed to show any individual simple dispersion regions. A qualitative explanation based on varying viscosities of the components of the solvent, the presence of polar radicals in the solute molecules, and the extensive association of the solute is offered.

EVIDENCE is becoming more convincing that the viscosity affecting the rotation of dipole molecules in an alternating field, referred to as microscopic viscosity, is not the same as that measured by the ordinary method, known as macroscopic viscosity.

The determination of microscopic viscosity by means of dielectric constant measurements is based upon the theoretical work of Debye on anomalous dispersion, the decrease in dielectric constant with increasing frequency. A large absorption of energy occurs simultaneously with anomalous dispersion.

In an alternating electric field four things increasingly oppose the turning of molecular dipoles. These are: Increasing viscosity, increasing particle size, increasing frequency, and decreasing temperature, the last due largely to its effect on the viscosity.

The effect of these factors is to throw the orientation of the molecules out of phase with the applied field. It is this lagging of the molecules behind the field that causes the great absorption of energy in the region of anomalous dispersion.

* Rewritten from a thesis by G. Harlowe Evans in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

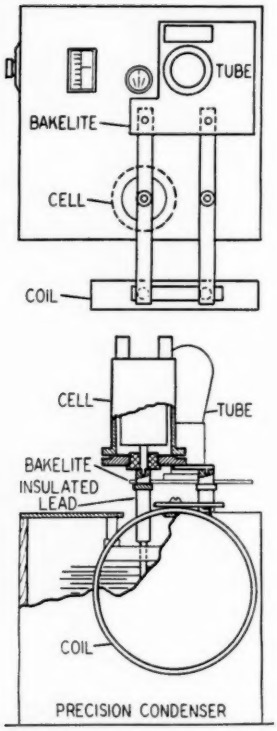

FIG. 1. Cell and receiver assembly.

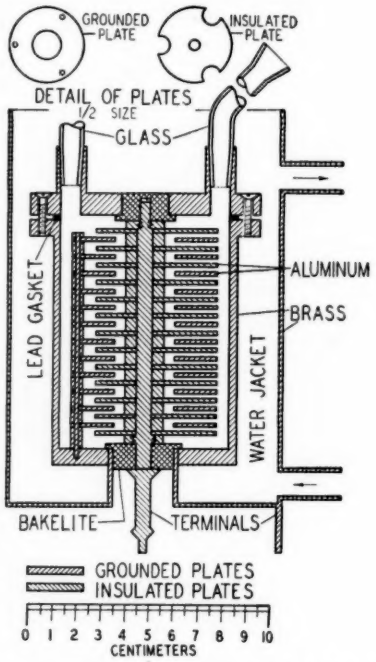

FIG. 2. The dielectric constant cell No. 3.

It thus appears that by measurements of dielectric constants in the region of anomalous dispersion one should be able to measure the viscosity which is really involved in the turning of the dipole molecules.

Measurements of this kind are reported in the literature for extremely large molecules of uncertain molecular weight in fairly fluid solvents[1, 2, 3] and also for small well-defined molecules in very viscous solvents.[4, 5] However, no information seems to be available on systems of molecules of large but definite molecular weight in solvents of moderately high viscosities. It was the original purpose of this investigation to study the relation between microscopic and macroscopic viscosity in such a system.

Solutions of lecithin (molecular weight 804) in Sun Oils S. A. E. 30, 40, 50, and 60 were found to possess the required characteristics. These oils are unusually pure and cover the viscosity range from 3.66 to 21.5 poises at 25°C. For Sun Oils 30, 40 and 60, 10 percent solutions were used, while for Sun Oil 50 two solutions containing 3 percent and 10 percent were employed.

With these solutions dielectric constants were measured at six frequencies and at three temperatures. The results allow a study of the influence of viscosity, temperature and concentration on the dielectric constant.

The values of ϵ_0 (the dielectric constant at optical frequencies) were obtained from refractive indices measured by means of an Abbe refractometer, making use of the Maxwellian relation $n^2 = \epsilon$ where n is the refractive index. Assuming that 300,000 meters (1000 cycles) is a long enough wavelength, values of ϵ_∞ (the so-called "static" dielectric constant) were determined at this wavelength by means of a precision Wheatstone bridge assembly developed by Mr. R. D. Thompson in this laboratory.

The values of ϵ' (the measured dielectric constant) at wavelengths of 32.8 m, 94 m, 320 m, 1308 m were calculated from capacitance measurements made by the substitution method employing a simple "voltage tuning" resonance apparatus very similar in electrical arrangement to

[1] J. Wyman, Jr., J. Biol. Chem. **90**, 443 (1931).
[2] N. Marinesco, J. chim. phys. **27**, 454 (1930); **28**, 51 (1931); Comptes rendus **192**, 625 (1931).
[3] J. Errera, J. chim. phys. **29**, 577 (1932).
[4] Goldammer-Sack, Physik. Zeits. **31**, 224 (1930).
[5] R. Luthi, Helv. Phys. Acta **6**, 139 (1933).

one used previously by Malone[6,7] in this laboratory. Malone found this to be the most suitable method of determining the dielectric constants of small amounts of liquids over a wide range of wavelengths.

For the voltage-tuning resonance method at high frequencies, Lattey[8] has summarized the sources of error which should be eliminated or for which corrections should be made. These are: (1) The conductance of the dielectric or leakage, (2) the earth capacitance, (3) the resistance of the leads, (4) the capacitance of the leads and (5) the inductance of the leads.

In the present work these sources of error were greatly reduced by the design of the apparatus, Fig. 1. The earth capacitance was very largely removed by the design of the measuring cell. Except for the small Bakelite insulator, the cell, Fig. 2, was constructed entirely of metal and provided with a water jacket for temperature control. During measurements the outer plate is connected to the ground and only the electric field through the insulator can cause an earth capacitance.

The errors due to resistance were practically eliminated by the use of heavy brass strips for all leads in the resonance circuit. The errors due to capacitance and inductance were reduced to a minimum by making the leads as short as possible, especially those connecting the cell and the precision condenser. Reference to Fig. 1 will indicate how these objectives have been attained.

By the substitution method used, the capacitance C_x* is obtained as the difference in readings on the precision condenser at the resonance points when the measuring cell is in the circuit and when it is out. The differences are obtained by a method similar to that described by Malone.[6]

It was found that the apparent capacitance of the empty cell changes with wavelength, being noticeably larger at longer wavelengths. One might expect that the capacitance of the cell full of liquid would increase in approximately the same ratio as that of the empty cell so that the relation $\epsilon' = C_x/C_a$ would be maintained. However, the dielectric constants calculated thus are too small indicating that the measured capacitance of the empty cell is too large. This is probably due to the unavoidable presence at some point, in any cell which might be used, of an insulating material having a greater dielectric constant than air, its relative effect being greater when the condenser is empty.

A test using benzene and carbon disulphide, however, showed that the relation

$$C_C/C_B = \epsilon_C'/\epsilon_B' = \text{a constant}$$

was independent of frequency. Here C_C and C_B are differences in condenser readings for carbon disulphide and benzene, non-polar liquids of known dielectric constants ϵ_C' and ϵ_B', respectively. Since the dielectric constants measured in this work were intermediate between those of benzene and CS_2, it was assumed that the relation would apply in all such measurements. As a generalized expression $\epsilon_x' = (C_X/C_B)\epsilon_B'$ was used for the unknown material. A further confirmation of this relation was later furnished by the fact that the dielectric constants of Sun Oil 30 calculated therefrom were constant throughout the wavelength range employed.

The values for ϵ' at the four intermediate wavelengths are plotted to scale against wavelength in Figs. 3–7. The values at the two extreme wavelengths spoken of earlier are also shown but are not plotted to scale horizontally. That these curves represent portions of true but not simple dispersion regions can be best shown by an analysis of a set of theoretical dispersion curves, Fig. 8. For curve B the assumed values were $\epsilon_0 = 2.46$, $\epsilon_\infty = 2.60$ and $\tau = (4/\pi)\times 10^{-6}$. Other necessary data appear on the figures. The effect of temperature, largely due to resulting changes in viscosity, is shown by a comparison of curves A, B and C. The density change with temperature is insignificant, but the change in viscosity η_i is very great if it is assumed that the temperature effect is roughly the same on microscopic as it is on macroscopic viscosity. The viscosity ratios $\eta_{50°} : \eta_{25°} : \eta_{18°} = 0.1 : 1 : 2$ used for the curves are approximately those for the macroscopic viscosi-

[6] Malone-Ferguson-Case, J. Chem. Phys. **1**, 836 (1933).
[7] R. Gunn, Phil. Mag. **48**, 224 (1924).
[8] Lattey-Gatty, Phil. Mag. **7**, 985 (1929).
* Since the relation between capacitance and condenser readings is linear over the range employed, differences in readings were used in all calculations rather than actual capacitances.

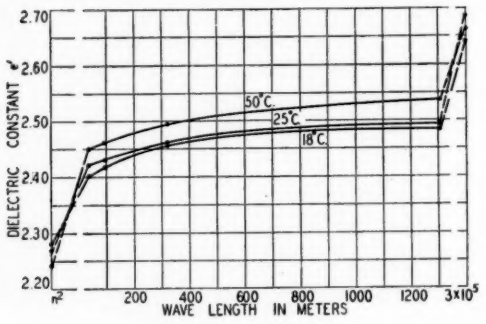

FIG. 3. Dispersion curves. Sun Oil 30 containing 10 percent lecithin.

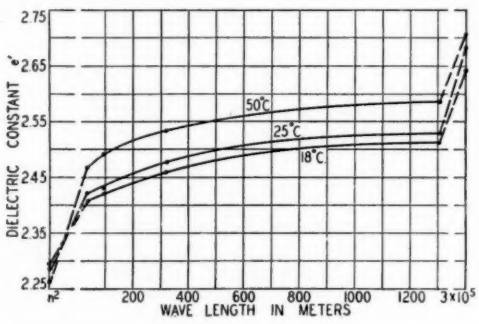

FIG. 6. Dispersion curves. Sun Oil 50 containing 10 percent lecithin.

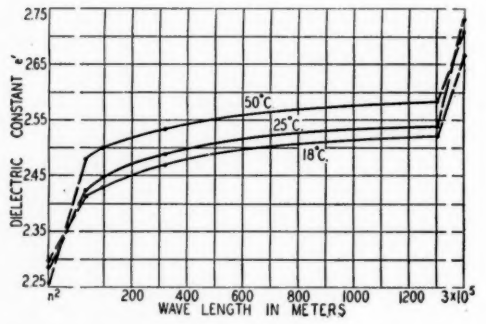

FIG. 4. Dispersion curves. Sun Oil 40 containing 10 percent lecithin.

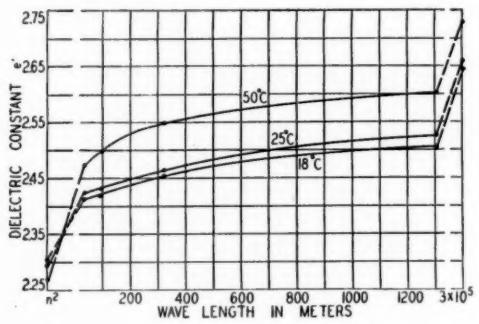

FIG. 7. Dispersion curves. Sun Oil 60 containing 10 percent lecithin.

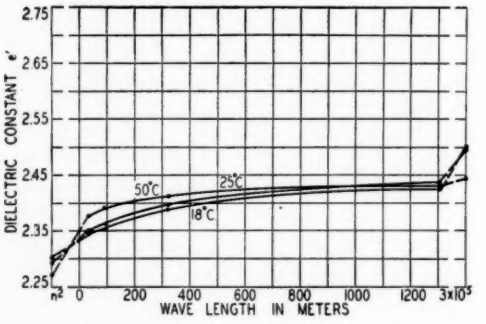

FIG. 5. Dispersion curves. Sun Oil 50 containing 3 percent lecithin.

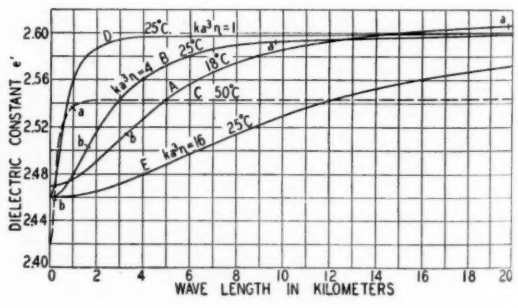

FIG. 8. Theoretical dispersion curves.

ties of Sun Oil 30. The values of ϵ_0 chosen were 2.47 at 18° and 2.42 at 50°. In obtaining these values it was assumed that the effect of temperature on ϵ_0 was the same as that measured for n^2 for the solutions.

Curves D, B and E show the effect of change in particle size or in viscosity at constant temperature. As seen in the figure the values of a^3 for these three curves are in the ratios of 1 : 4 : 16.

It will be seen that in the region of low wavelengths in all cases the values of ϵ' are small and approach ϵ_0. In the high wavelength region the values of ϵ' are large and very rapidly become constant. In each of these regions the temperature coefficient of the dielectric constant is negative (curves A, B and C). However, in the region of dispersion the temperature coefficient is decidedly positive. Thus the general effect of in-

creasing the temperature is to shift the whole curve to somewhat lower values of dielectric constants and to considerably lower wavelengths. For instance, on curve A, by increasing temperature, the points (a) and (b) are shifted to the corresponding positions indicated on curves B and C. The effect of increasing either the size a^3 of the particles or the viscosity η_i of the solvent is to shift the whole curve to higher wavelengths, as shown by curves B, D and E. In the light of these theoretical curves it can be shown that Figs. 3–7 represent the behavior of materials which are dispersing.

On examination of Figs. 3, 4, 6 and 7 it is seen that the temperature coefficient is always negative for the values of $\epsilon_0 = n^2$, while for the value ϵ' at wavelengths from 32.8 m to 1308 m it is positive in all cases. Thus there is a complete reversal of the magnitude of ϵ' with temperature. This is characteristic of the lower end of dispersion curves as will be seen in Fig. 8. Again, it is observed that the values of ϵ' for the two less viscous solutions (S. A. E. 30 and 40) at 1036 cycles (the extreme upper value) and 50° have dropped below the corresponding values at 25° and that while the corresponding value for the S. A. E. 50 solution has approached the value at 25°, it has not yet dropped below it. The corresponding value for S. A. E. 60 solution has maintained its relative position.

These reversals for the less viscous solutions would indicate that the values at 1036 cycles are either near or upon the upper plateau of the dispersion curves. From an examination of the theoretical curves, Fig. 8, it would be expected that the less viscous solutions at the highest temperatures would reach the top of the curve at lower wavelengths while the more viscous solutions would approach it at higher wavelengths. There is no indication in the range covered of the value at 25° on any of the curves tending to drop below that for 18°.

The apparent discrepancy in the height of corresponding curves for the different oils is due to the difference in the dielectric constants of the pure oils. When corrections for the latter are made the curves for the different solutions at the same temperature assume their expected relative positions. Furthermore, the magnitude of these shifts is of the right order since the change in viscosity from one oil to the next is less than the change in viscosity of any one oil due to temperature in passing from 18° to 25°.

In Fig. 5 for the 3 percent solution, dispersion is shown even more definitely by the fact that the order is completely reversed not only between optical frequencies and 32.8 m but also at the other end of the curves. In fact, the curve for 50° begins to approach that for 25° between 200 and 300 m, crossing it at about 1000 m and falling much below even those for 18° at 1036 cycles (289,570 m).

The fact that the value of ϵ' at 25° has dropped below that for 18° at 1036 cycles indicates, also, that for this concentration dispersion occurs at lower wavelengths than for the higher concentration.

Since the temperatures are the same and the viscosities greater than those of the Sun Oil 30 and 40 solutions, the lowered dispersion range must be ascribed, in accordance with the Debye theory, at least, to the presence of smaller particles. This clearly indicates association of the lecithin molecules. These phenomena all indicate distinct dispersion, but it must be admitted that considering the rapid dispersion at low wavelengths the dispersion covers too great a range to be a simple dispersion region.

It becomes evident that it is desirable to obtain a larger number of points on the curve for one solution and to extend the measurements to longer wavelengths in order to determine the possibility of the presence of irregularities in the curve indicating the presence of simple overlapping dispersion curves.

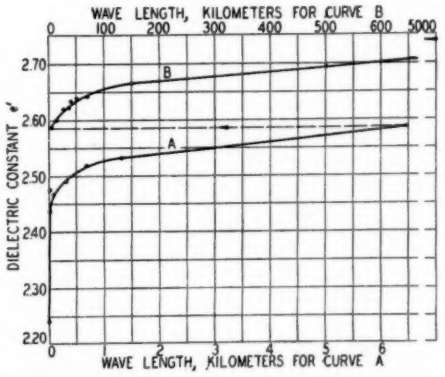

FIG. 9. Dispersion curve. Sun Oil 3 containing 10 percent lecithin, at 50°C.

The system used for this extended work was a solution containing 10 percent lecithin in Sun Oil 30 at 50°C. A set of measurements was made throughout the whole wavelength range on benzene and also on pure Sun Oil 30. The value at all frequencies for Sun Oil 30 was 2.293 ± 0.003.

The curve of Fig. 9 is a plot of the data obtained.* Curve *B* represents the entire range of wavelengths down to 6450 m while curve *A* shows the lower portion from 6450 m to zero meters expanded horizontally 100-fold.

Even with these more extensive and precise data no evidence is obtained of separate dispersion regions. As a matter of fact, except for the two extreme points at zero and infinite wavelengths the dielectric constant is found to be, within experimental error, a linear function of the logarithm of the wavelength and is represented by

$$\epsilon' = 2.324 + 0.0619 \log \lambda.$$

When the complex nature of the systems is considered the absence of the appearance of single dispersion regions is not surprising. Any one of the oils is doubtless a complex mixture of molecules of various sizes. The viscosity of each individual component is probably different and thus the relaxation time of a given polar molecule caused by each would be different. The resulting dispersion curve would therefore be a summation of several simple dispersion regions.

It has been suggested by Race[10] and by Luthi[5] that polar radicals within the molecule as well as the molecule as a whole might cause dispersion. Lecithin is supposed to consist of several long chain compounds joined together in one large molecule. The molecule as a whole would cease to orient at very long wavelengths, and the various radicals would cease with frequency in the order of their size, each having a different relaxation time. This likewise would result in a complex dispersion curve. Either or both of these explanations could account for the lower portion of the dispersion curves obtained.

The upper portions of the complex dispersion curves may be caused by the presence of associated groups of different sizes. It was shown in the discussion of Fig. 5 that lecithin is highly associated. These associated particles might readily approach colloidal dimensions and thus possess long relaxation periods.*

Recently several other investigators have obtained dispersion curves which failed to show discrete dispersion regions. Among these may be mentioned Kitchin,[11] Race [10] and Williams[12] each of whom experienced difficulty in the interpretation of the data obtained in terms of the Debye theory. In some cases the difficulty doubtless would have been enhanced if a wider frequency range had been covered. Williams states "In conclusion, it may be said that these results show that the Debye theory, although theoretically sound, is very difficult to apply quantitatively to the existing dielectric constant data. . . . At the present time it does not seem readily possible to obtain monodisperse systems either of large molecules or of particles of colloidal size, in nonpolar solvents."

Among the unique features of the present investigation are: (1) The design and assembly of the cell and receiver to minimize various errors present in such measurements, (2) the large number and extremely wide range of wavelengths employed, (3) the type of solute-solvent system employed, and (4) the relatively large change of dielectric constant with frequency for such viscous solutions.

* The value at 39.2 m is obviously in error, but circumstances made it impossible to recheck it after plotting the curve.

[10] H. H. Race, J. Phys. Chem. **36**, 1928 (1932).

* An approximate calculation shows that associated particles of about 1000 molecules are sufficient to account for the dispersion at the upper end of the curve.

[11] D. W. Kitchin, J. Ind. and Eng. Chem. **24**, 549 (1932).

[12] Oncley-Williams, Phys. Rev. **43**, 341 (1933).

The Kinetics of the Decomposition of Gaseous Glyoxal

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(Received January 31, 1935)

The decomposition of gaseous glyoxal has been investigated from 410° to 450°C. The reaction is homogeneous and first order. Considerable carbon and tar is deposited, however, and the results are erratic. The following three reactions occur to about the same extent:

$$\mathrm{CHO-CHO=2\,CO+H_2},$$
$$\mathrm{CHO\ \ CHO=C+CO+H_2O},$$
$$\mathrm{CHO\ \ CHO=\frac{1}{n}\,(CHO-CHO)_n}.$$

The results are discussed from the point of view of the occurrence of glyoxal as an intermediate in the oxidation of acetylene.

GLYOXAL has frequently been postulated as a product of the oxidation of gaseous organic compounds. It has been definitely shown to be present in considerable quantities during the oxidation of acetylene.[1] It has been suggested that the primary step in the acetylene oxidation is the formation of glyoxal, which then either oxidizes further or decomposes. Although, as far as we are aware, no investigation of the thermal decomposition has ever been made, it has always been assumed that it occurs as follows:[2]

$$\mathrm{CHO-CHO=CO+HCHO},$$
$$\mathrm{HCHO=CO+H_2},$$

giving the overall reaction

$$\mathrm{CHO-CHO=2\,CO+H_2}.$$

The present investigation was therefore undertaken (a) because of the interest attaching to the decomposition of simple molecules, (b) to fill an experimental gap in the Bone "hydroxylation" scheme for the oxidation of gaseous organic compounds, and (c) in connection with an investigation of the acetylene oxidation now in progress in this laboratory.

EXPERIMENTAL

Rates of reaction were followed by admitting the reactants to a heated Pyrex bulb, and observing the rate of pressure increase at constant volume by means of a capillary manometer. The apparatus was similar to one which has been previously described.[3] The reaction vessel was heated by means of an electric furnace, the temperature being controlled by the hand regulation of rheostats. The temperature could be maintained constant to within 0.5°C. Temperatures were measured with a chromel-alumel thermocouple in conjunction with a thermocouple potentiometer. The connecting tubing between the reaction vessel and the manometer was maintained at 100°C by means of an electrical heating element to prevent condensation.

The preparation of pure gaseous glyoxal is complicated by the fact that it polymerizes readily to solid paraglyoxal, and the polymerization is not directly reversible. The gas was prepared in the usual way by heating paraglyoxal (Schuchardt) with phosphorus pentoxide.[4] Considerable dehydration and charring occurs, however, and the gas is contaminated with a large amount of carbon monoxide. It was found that if the gas were condensed at −80° it froze out as the monomer, and it was possible to pump off foreign gases. If the solid monomer were heated to room temperature for a short time it evaporated with very little polymerization. During the course of the investigation the glyoxal was therefore stored as a solid at −80°, and was only warmed up when a sample of gas was to be withdrawn. Blank experiments showed that no com-

[1] Kistiakowsky and Lenher, J. Am. Chem. Soc. **52**, 3785 (1930); Spence and Kistiakowsky, ibid. **52**, 4837 (1930); Lenher, ibid. **53**, 2962 (1931).

[2] See, for example, the reference 1 and also Bone, Proc. Roy. Soc. **A137**, 243 (1932); J. Roy. Soc. Arts **81**, 550 (1933).

[3] Hatcher, Steacie and Howland, Can. J. Research **7**, 149 (1932).

[4] Harries and Temme, Ber. **40**, 165 (1907).

plication was introduced by polymerization in the connecting tubes.

It should be mentioned at the outset that the reaction is complicated by the deposition of carbon, tar, etc., and that in consequence the results obtained are rather erratic. It is therefore impossible to investigate the reaction with very high accuracy, but sufficient results have been obtained to establish the main features of the process.

The Products of the Reaction

If the reaction proceeds according to the mechanism given above, we should have a pressure increase of 200 percent at completion, since formaldehyde would decompose at the temperatures used. Actually, however, the average pressure increase at completion was about 90 percent. Some typical values are given in Table I.

Table I. *The pressure increase accompanying the reaction.*

Temp. (°C)	Percent pressure increases
450	93.0, 83.8, 85.3, 103.0, 94.5, 86.6
440	87.4, 93.2, 89.4, 92.5, 93.2, 94.0, 101.2, 94.7
430	73.5, 71.1
420	82.2

The gaseous products of the reaction were analyzed in a Burrell gas analysis apparatus, hydrogen being determined by combustion. Almost all the condensable substances (glyoxal, water, etc.) condensed out in the process of sampling. A small amount of material (always less than 1 percent) was absorbed in the KOH burette. It is very unlikely that this could be carbon dioxide, and it was assumed to be a trace of glyoxal or other condensable material. In any event the error which might be involved is negligible. In order to refer the gaseous products found back to the initial amount of glyoxal from which they came, it is necessary to know the amount of condensable material present in the mixture being sampled. This was done in the usual way by adding a known amount of nitrogen to the glyoxal before the reaction, and then determining nitrogen in the gaseous products. The results of analyses of this kind are given in Table II.

The main conclusion to be drawn from the table is that the gaseous products of the reaction consist entirely of hydrogen and carbon monoxide, the amount of carbon monoxide being much greater than that of hydrogen. With decreasing temperature the H_2/CO ratio decreases to some extent. The carbon monoxide formed is approximately equal to the glyoxal disappearing.

In the case of analyses at the half-way stage it is difficult to draw conclusions regarding the amount of condensable material formed, on account of the uncertainty as to how much glyoxal has decomposed. At completion, however, it is possible to deduce the amount of condensable products with fair accuracy. At 450°C the amount is only slightly greater than that of hydrogen, while at 430° it is more than twice as much. The significance of this will be discussed later.

It is possible from the above analytical data to draw up a material balance for C, H and O, and hence to deduce the composition of the condensable material. Too much reliance cannot be placed in such balances, since all the errors involved in the reaction measurements and analyses accumulate in the result. If such a balance is made for all the analyses at completion, we obtain for the average composition of the condensable products

$$C_{1.00}H_{1.23}O_{1.00} \quad \text{at} \quad 450°C,$$

and

$$C_{1.00}H_{1.28}O_{1.00} \quad \text{at} \quad 430°C.$$

Or, on the average,

$$C_{1.00}H_{1.26}O_{1.00}.$$

The Mechanism of the Reaction

It has previously been assumed[2] that the glyoxal decomposition proceeds simply as

$$CHO-CHO=CO+HCHO=2\,CO+H_2, \quad (1)$$

formaldehyde being completely decomposed at the temperatures used. It is obvious that such a simple scheme cannot hold, since (a) carbon and tar are formed, (b) the pressure increase at completion is only 90 percent instead of 200 percent, (c) a large amount of condensable products are formed, (d) the H_2/CO ratio is only 0.2 to 0.3 instead of 0.5.

Other obvious possibilities are:

TABLE II. *The products of reaction.*

Temp. (°C)	% pressure increase when sample was taken	Moles per 100 moles initial glyoxal (including unchanged glyoxal, if any) CO	H_2	Condensable	H_2/CO	
450	50	41.6	15.0	93.4	0.36	0.34
450	50	46.0	17.1	86.9	0.37	
450	50	48.6	14.3	87.1	0.29	
450	Completion	94.2	41.5	48.1	0.44	0.39
450	"	107.6	30.9	56.0	0.29	
450	"	90.0	40.3	56.3	0.45	
430	50	56.8	14.7	78.5	0.26	0.29
430	50	54.0	16.7	79.3	0.31	
430	Completion	85.6	21.6	66.3	0.25	0.29
430	"	78.0	25.4	67.7	0.33	
410	50	46.8	10.7	92.5	0.23	0.23
410	50	57.6	13.3	79.1	0.23	
410	50	54.6	11.9	83.5	0.22	

$$CHO-CHO=C+CO+H_2O, \quad (2)$$
$$CHO-CHO=(1/n)(CHO-CHO)_n, \quad (3)$$

where $(CHO-CHO)_n$ represents a polymer or condensable substance or substances of higher molecular weight than glyoxal, with approximately the same empirical composition.

It is not possible to account for the gaseous products on the basis of reactions (2) and (3) alone. On account of the fact that both CO and H_2 are formed, it appears probable that reaction (1) occurs to a considerable extent. A simple combination of (1) and (2) could be made to yield the correct H_2/CO ratio, but such a combination would give a pressure increase far too high (about 150 percent). A simple combination of (1) and (3) would give the correct pressure increase, but could not yield a H_2/CO ratio very different from 0.5.

Provided that reaction (3) gives rise to little gaseous material, a combination of reactions (1), (2) and (3) will account satisfactorily for the experimental results. Thus if we assume that all three reactions occur to the same extent, we have for the overall reaction

$$3\,CHO-CHO=3\,CO+H_2+C+H_2O+(1/n)(CHO-CHO)_n.$$

This accounts for the main facts, thus:

(a) The CO formed is equal to the glyoxal decomposing,
(b) The H_2/CO ratio is 0.33,
(c) If we assume that n is about 3, the pressure increase at completion will be approximately 80 percent,
(d) The composition of the condensable product is
$C+H_2O+C_2H_2O_2=C_{1.00}H_{1.33}O_{1.00}$,
which is in good agreement with experiment.

It appears therefore that the three reactions are of about equal importance.

An investigation of the photochemical decomposition of glyoxal has been carried out.[5] The reaction was bimolecular, about 1.5 percent of the initial glyoxal decomposing to CO and H_2, and the remainder yielding CO and glycerosone ($C_3H_4O_3$). This is essentially a polymerization, similar to reaction 3, but splitting out CO. Norrish and Griffiths state that glycerosone decomposes at 200°C. Hence it is not likely that it is of importance here. It is, however, possible to account for the experimental results on the basis of a mechanism such as:

$$(1') \qquad C_2H_2O_2 \rightarrow 2\,CO+H_2,$$
$$(2') \qquad 2_6C_2H_2O_2 \rightarrow C_3H_4O_3+CO,$$
$$(3') \qquad C_3H_4O_3 \rightarrow \text{polymer (tar)}.$$

Considering the fact that large amounts of carbon are deposited, in addition to tarry materials, the first mechanism seems much more plausible.

The diminution of the H_2/CO ratio with decreasing temperature and the corresponding increase in the proportion of the condensable products must be due to a change in the balance between reactions 1 and 2, reaction 1 predominating at the higher temperature.

[5] Norrish and Griffiths, J. Chem. Soc. **1928**, 2829–40.

The Rate of Reaction

In view of the complicated nature of the reaction as outlined above, and of the fact that carbon and polymerized materials are formed, it is hardly to be hoped that the kinetics of the reaction can be very accurately established. Actually, the results obtained are decidedly erratic. It is possible, however, to infer the main characteristics of the reaction with some certainty.

The complete data for a typical experiment are given in Table III. It will be seen that excellent first order constants are obtained. This was invariably true throughout the investigation, in spite of the erratic nature of the absolute rate.

Table III. *Data for a typical experiment.*

Temperature 440°C			*Empty reaction vessel*	
Time (min.)	Pressure (cm)	Pressure increase (cm)	Percent reaction	K (first order), min.$^{-1}$
0	11.70	0.00	0.0	—
1	12.70	1.00	9.2	0.041
2	13.70	2.00	18.4	0.044
3	14.60	2.90	26.6	0.045
5	16.10	4.40	40.5	0.045
7	17.30	5.60	51.5	0.045
10	18.80	7.10	65.3	0.046
13	19.80	8.10	74.4	0.046
18	21.00	9.30	85.4	0.046
25	21.80	10.10	92.8	0.046
30	22.10	10.40	95.5	0.045
35	22.30	10.60	97.3	0.045
40	22.50	10.80	—	—
45	22.60	10.90	—	—
55	22.60	10.90	—	—

The effect of temperature and of the glyoxal pressure on the rate of reaction is shown by Table IV. As a measure of the rate we have used $T_{12.5}$ and T_{25}, i.e., the times for the pressure to increase by 12.5 and 25 percent, respectively.

On account of the erratic nature of the results, it is not possible to determine the activation energy with any degree of accuracy. From the mean values of $T_{12.5}$ and T_{25} at higher pressures we obtain the value $E=54{,}000\pm10{,}000$ cals.

It will be seen from Table IV that the times for a given fractional pressure increase are roughly independent of the initial pressure, and hence the reaction is apparently first order, insofar as the effect of pressure on the rate is concerned. The results, however, are too erratic to permit of accurate conclusions.

The last 7 runs listed above were made in a vessel packed with short lengths of 3/16 inch Pyrex tubing, the surface-volume ratio being about three times greater than that for the empty bulb. It is apparent that packing the bulb has very little influence on the rate, and the reaction is therefore homogeneous.

Discussion

As we have seen, the results are rather erratic, and the reaction is far from an ideal one from the

Table IV. *Reaction rate data.*

Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25}, (min.)	Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25}, (min.)	Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25}, (min.)	Initial pressure, (cm)	$T_{12.5}$, (min.)	T_{25}, (min.)
Empty vessel.....410°C						16.55	1.7	3.6	7.95	1.3	3.3
17.15	4.6	10.8	10.95	7.5	14.6	13.30	1.3	2.8	6.30	2.3	4.4
14.10	7.6	15.8	9.55	6.8	14.6	13.05	1.2	2.7	4.75	2.0	3.7
12.70	9.6	20.3	7.85	5.9	13.3	11.70	1.5	3.0	4.45	3.3	6.0
11.65	9.1	20.1	6.90	8.5	17.2	10.30	1.5	3.2	4.30	2.9	6.3
Empty vessel.....420°C						9.90	1.4	2.8			
11.55	7.0	14.6	9.05	7.4	15.0	*Empty vessel.....450°C*					
10.30	6.4	13.5	7.80	5.8	13.4	22.15	0.6	1.4	10.0	1.2	2.5
9.95	5.8	12.1	6.40	7.6	—	21.70	1.1	2.2	4.05	1.8	4.3
Empty vessel.....430°C						15.50	1.1	2.4	3.30	1.4	3.3
20.85	2.1	4.2	10.65	2.9	6.6	10.40	1.1	2.2			
17.45	2.5	5.3	8.40	3.0	7.4	*Packed vessel.....430°C*					
16.05	3.4	7.4	5.90	2.6	9.3	18.55	4.1	7.9	13.70	2.9	6.4
Empty vessel.....440°C						15.10	2.3	5.1	11.35	2.8	6.3
20.60	1.4	2.1	8.30	1.1	3.0	*Packed vessel.....450°C*					
17.75	1.1	2.4	8.05	1.9	4.6	12.45	1.0	2.1	7.90	0.7	1.6
						10.60	1.2	2.8			

kinetic standpoint. The main interest in the results, however, lies in the fact that previous assumptions regarding the simple nature of the glyoxal decomposition have been shown to be incorrect.

In the oxidation of acetylene no appreciable quantity of carbon or tar is formed.[1, 6] It therefore follows that while glyoxal may be formed and *oxidized* in the acetylene oxidation, it cannot *decompose* during the course of this reaction as has been previously assumed.

It also follows that the scheme proposed by Lenher for the oxidation of acetylene catalyzed by the oxides of nitrogen, *viz.*:

$$C_2H_2+O_2=CHO-CHO\rightarrow(CHO-CHO)_3$$
$$\searrow$$
$$CO+HCHO$$
$$\downarrow +O_2$$
$$CO+CO_2+H_2O,$$

is not a possible mechanism, although certain *ad hoc* modifications could be made to bring it into line with the present work.

An investigation of the glyoxal oxidation is in progress.

[6] Steacie and McDonald, unpublished work.

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Orientation Effects in Bimolecular Ionic Reactions

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It is shown on the basis of accepted views concerning second order ionic reactions in solution that the variation with concentration of the electrostatic orientation effects in such a reaction arising from the lack of symmetry of a spheroidal ion is negligible in dilute solution. Deviations from Brönsted's law must be attributed to other causes.

IT has been observed that certain bimolecular ionic reactions deviate very considerably from the requirements of the limiting Brönsted formula, which is, for water as solvent and at 25°C,

$$\log k''=\log k_0+z_1z_2(\mu)^{\frac{1}{2}}. \quad (1)$$

In this equation k'' is the observed bimolecular specific reaction rate, k_0 is a quantity independent of concentration, z_1, z_2 are the valences of the reacting ions, and μ is the ionic strength. In many instances these deviations are probably due to failure of the simple Debye-Hückel limiting law for ions of high valence, but there are a few cases where this explanation cannot hold. Outstanding among these is the one observed by LaMer and Kamner.[1] These authors found that the reaction between α-brompropionate and thiosulfate ions follows the Brönsted formula accurately, while the analogous reaction involving the β-brompropionate ion leads to a slope of the $\log k''$ *vs.* $(\mu)^{\frac{1}{2}}$ curve which does not even have the expected sign. After an exhaustive study had indicated that the effect is not due to side-reactions or other such causes, LaMer and Kamner suggested that purely electrostatic effects resulting from a comparatively large separation of charge and center of reaction (the bromine atom) in the unsymmetrical organic ion might lead to the observed results. It is the purpose of the present note to examine this suggestion a little more closely. It will appear from the study of a fairly general case that this explanation is not valid, if one accepts present views concerning second order ionic reactions in solution.

Christiansen[2] developed a statistical theory of bimolecular ionic reactions which he showed to be in formal agreement with Eq. (1) in very dilute solutions. His treatment led to a general result which may be written

$$k''=k_0\exp(-\epsilon z_2\varphi_1/kT)\cdot\Omega\cdot(1+\Sigma\chi_i\zeta_i). \quad (2)$$

[1] LaMer and Kamner, J. Am. Chem. Soc. **53**, 2832 (1931).

[2] Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

The term in parentheses expresses an approximation to the effect of deactivating collisions, and may be considered as practically independent of concentration at low total concentrations. Ω is a factor introduced to allow for orientation effects, and was also considered by Christiansen to be independent of concentration in very dilute solutions. The quantity φ_1 is the electrostatic potential due to an ion of type 1 and its atmosphere, at a distance r from its point charge ϵz_1; r is to be taken as the separation of the charges of the ions at the moment of reaction. Christiansen used for the value of φ_1 the value obtained by Debye and Hückel[3] for spherically symmetrical ions of negligible diameter in a solution of low ionic strength,

$$\varphi_1=(\epsilon z_1/Dr)e^{-\kappa r}\approx-\epsilon z_1\kappa/D+(\epsilon z_1/Dr)(\kappa r\ll 1). \quad (3)$$

D is the dielectric constant of the medium and κ is defined by

$$\kappa^2=(\pi\epsilon^2 N/125DkT)\mu, \quad (4)$$

N being Avogadro's number.

Eq. (2) will be used as the basis of an extension to the case that the ions of type 1 are not spherically symmetrical. In order to make the treatment reasonably simple the ions of type 1 are assumed to be prolate spheroidal, with semiaxes a and b $(a>b)$. These dimensions define a spheroidal surface beyond which, on the average, the charges of the other ions in the solution do not penetrate. A coordinate system is taken with origin at the center of an ion of type 1, the semimajor axis of which lies along the z-axis. Then in the confocal coordinates, η, ϑ, φ, defined by the relations

$$\begin{aligned} x&=c\sinh\eta\sin\vartheta\cos\varphi \qquad 0\leqq\eta<\infty,\\ y&=c\sinh\eta\sin\vartheta\sin\varphi \qquad 0\leqq\vartheta\leqq\pi, \quad (5)\\ z&=c\cosh\eta\cos\vartheta \qquad 0\leqq\varphi<2\pi, \end{aligned}$$

the "surface" of the ion corresponds to $\eta=\eta_0$ such that

$$\cosh\eta_0=a/c;\quad \sinh\eta_0=b/c$$

where $2c$ is the separation of the foci. The point charge ϵz_1 is located at $(\eta', \vartheta', \varphi')$.

If ψ_1' is the potential inside the ion due to its atmosphere and ψ_1'' is that due to the charge ϵz_1, then the total potential for $\eta<\eta_0$ is $\psi_1=\psi_1'+\psi_1''$. Now ψ_1' satisfies Laplace's equation and is bounded at the origin, so that it has the form[4]

$$\psi_1'=\sum_{n=0}^{\infty}\sum_{m=0}^{n}P_n^m(\cosh\eta)P_n^m(\cos\vartheta)[C_{nm}\cos m\varphi+D_{nm}\sin m\varphi] \quad (6)$$

where the P_n^m are the associated Legendre functions of the first kind and the C_{nm}, D_{nm} are constants. Expansion[5] of the reciprocal of the distance between $(\eta, \vartheta, \varphi)$ and $(\eta', \vartheta', \varphi')$ gives

$$\begin{aligned} \psi_1''&=\sum_{n=0}^{\infty}\sum_{m=0}^{n}Q_n^m(\cosh\eta)P_n^m(\cos\vartheta)E_{nm}\cos m\varphi,\\ E_{n0}&=(2n+1)(\epsilon z_1/Dc)P_n(\cosh\eta')P_n(\cos\vartheta'), \qquad \eta>\eta' \quad (7)\\ E_{nm}&=(-1)^m 2(2n+1)(\epsilon z_1/Dc)[(n-m)!/(n+m)!]^2 P_n^m(\cosh\eta')P_n^m(\cos\vartheta')\cos m\varphi' \end{aligned}$$

if we take $\varphi'=0$. Here the Q_n^m are the associated Legendre functions of the second kind and D is the dielectric constant inside the ion, assumed to be the same as that of the surrounding medium.

The potential ψ_2 for $\eta>\eta_0$ is a solution of $\Delta\psi_2=\kappa^2\psi_2$. Assuming that $\psi_2=H(\eta)\Theta(\vartheta)\Phi(\varphi)$, we obtain

$$\Phi=\alpha\cos m\varphi+\beta\sin m\varphi, \qquad m=0, 1, 2, \cdots \quad (8)$$

$$(1-x^2)y''-2xy'+(k^2x^2+\mu-m^2/(1-x^2))y=0. \quad (9) \text{ and } (10)$$

In Eq. (9) $y=\Theta$, $x=\cos\vartheta$ and $-1\leq x\leq 1$; in Eq. (10) $y=H$, $x=\cosh\eta$, and $1\leq x<\infty$. m and μ are

[3] Debye and Hückel, Physik. Zeits. **24**, 185 (1923).
[4] Cf. Hobson, *Spherical and Ellipsoidal Harmonics*, Cambridge, 1931, p. 412.
[5] Hobson, reference 4, p. 416.

separation constants. Since the parameter $k=\kappa c$ is small, (9) and (10) may be treated by perturbation methods, taking $\mu=n(n+1)+0(k^2)$. We thus set

$$\Theta_n^m=\sum c_j P_j^m(\xi), \qquad \xi=\cos\vartheta, \qquad m=0, 1, 2, \cdots, n. \tag{11}$$

Using the formula

$$\xi^2 P_n^m=\frac{(n-m+2)(n-m+1)}{(2n+1)(2n+3)}P^m{}_{n+2}+\frac{2n^2+2n-1-2m^2}{(2n-1)(2n+3)}P_n^m+\frac{(n+m)(n+m-1)}{(2n-1)(2n+1)}P^m{}_{n-2}$$

we readily find that, aside from constant factors

$$\begin{aligned}\Theta_n^m&=P_n^m+k^2\left[\frac{(n-m+2)(n-m+1)}{2(2n+1)(2n+3)^2}P^m{}_{n+2}-\frac{(n+m)(n+m-1)}{2(2n-1)^2(2n+1)}P^m{}_{n-2}\right]+O(k^4)\\&=P_n^m+\alpha^m{}_{n+2}P^m{}_{n+2}+\beta^m{}_{n-2}P^m{}_{n-2}+O(k^4).\end{aligned} \tag{12}$$

An approximate solution of Eq. (10) can now be found by consideration of the unseparated equation involving $y=\Theta H$ as dependent variable. This equation is satisfied by

$$y=\sin^m\vartheta\,\sinh^m\eta\,e^{-k\cos\vartheta\cosh\eta}\equiv \mathrm{K}(\vartheta,\eta),$$

so that we have

$$H_n^m(\zeta)=\int_1^\infty \mathrm{K}(\xi,\zeta)\Theta_n^m(\xi)d\xi, \qquad \zeta=\cosh\eta. \tag{13}$$

We thus have to evaluate integrals of the type

$$I_n^m=i^m(\zeta^2-1)^{m/2}\int_1^\infty(\xi^2-1)^{m/2}e^{-k\zeta\xi}P_n^m(\xi)d\xi. \tag{14}$$

When ξ is not real and between -1 and $+1$,

$$P_n^m(\xi)=\frac{(n+m)!}{(n-m)!}P_n^{-m}(\xi)=\frac{(n+m)!}{(n-m)!}\frac{1}{2^n n!}(\xi^2-1)^{-m/2}\frac{d^{n-m}}{d\xi^{n-m}}(\xi^2-1)^n.$$

Introducing this relation into Eq. (14) and integrating m times by parts gives

$$I_n^m=i^m\frac{(n+m)!}{(n-m)!}\frac{(\zeta^2-1)^{m/2}}{(k\zeta)^m}\int_1^\infty e^{-k\zeta\xi}P_n(\xi)d\xi.$$

It can be shown that

$$\int_1^\infty e^{-k\zeta\xi}P_n(\xi)d\xi=\frac{i^{n+\frac{1}{2}}}{(k\zeta)^{\frac{1}{2}}}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}H^{(1)}{}_{n+\frac{1}{2}}(ik\zeta),$$

where $H^{(1)}{}_{n+\frac{1}{2}}$ is the Hankel function of the first kind,[6] and enters here because it is the only type of Bessel function which vanishes for infinite positive imaginary argument.

To complete the calculation of the solution of Eq. (10) it is necessary to extend the computation of the coefficient $\alpha^m{}_{n+2}$ in Eq. (12), since the fact that $H^{(1)}{}_{n+\frac{1}{2}}(ik\zeta)/H^{(1)}{}_{n+\frac{1}{2}}(ik\zeta)=O(1/k^2)$ necessitates the inclusion of more terms to obtain the desired accuracy. The result obtained is, omitting unessential constant factors,

$$H_n^m(\zeta)=\frac{(\zeta^2-1)^{m/2}}{(k\zeta)^{m+\frac{1}{2}}}\left[H^{(1)}{}_{n+\frac{1}{2}}(ik\zeta)+\sum_{j=1}^{\infty}(-1)^j a^m{}_{n,\,2j}H^{(1)}{}_{n+2j+\frac{1}{2}}(ik\zeta)\right]+\text{relative } O(k^4),$$

[6] The definition of $H_{n+\frac{1}{2}}^{(1)}$ used here is that given in Jahnke-Emde, *Funktionentafeln*, 2nd ed., Berlin, 1933, p. 202. In evaluating the potential about a spherical ion the point charges of which are not located at its center, Kirkwood (J. Chem. Phys. **2**, 599 (1934)) was led to the functions $e^{-\kappa r}K_n(\kappa r)r^{-n-1}$ where the K_n are polynomials. These functions are identical, aside from constant factors, with the functions $r^{-\frac{1}{2}}H_{n+\frac{1}{2}}^{(1)}(i\kappa r)$.

$$a^m{}_{n,\,2j}=k^{2j}\frac{(n+m+1)(n+m+2)\cdots(n+m+2j)}{2\cdot4\cdots(2j)(2n+1)(2n+3)^2(2n+5)^2\cdots(2n+2j+1)^2(2n+2j+3)\cdots(2n+4j-1)}$$
$$\times\left[1+\frac{2jk^2(4m^2-1)}{(2n-1)(2n+3)^2(2n+4j+3)}\right]+\text{relative } O(k^4). \quad (15)$$

The general expression for the potential outside the ion is taken in the form

$$\psi_2=\sum_{n=0}^{\infty}\sum_{m=0}^{n}H_n{}^m(\cosh\eta)\Theta_n{}^m(\cos\vartheta)[A_{nm}\cos m\varphi+B_{nm}\sin m\varphi]. \quad (16)$$

The coefficients A_{nm} and B_{nm} may be calculated from the boundary conditions that

$$\psi_1=\psi_2 \quad\text{and}\quad \nabla\psi_1=\nabla\psi_2 \quad\text{at}\quad \eta=\eta_0. \quad (17)$$

We thus find that

$$A_{nm}=E_{nm}\left\{\frac{\dfrac{d}{d\zeta}\dfrac{Q_n{}^m}{P_n{}^m}}{\dfrac{d}{d\zeta}\dfrac{H_n{}^m}{P_n{}^m}}\right\}_{\zeta=\zeta_0}-\alpha_n{}^mE_{n-2,\,m}\left\{\frac{\dfrac{d}{d\zeta}\dfrac{Q^m{}_{n-2}}{P^m{}_{n-2}}\cdot\dfrac{d}{d\zeta}\dfrac{H^m{}_{n-2}}{P_n{}^m}}{\dfrac{d}{d\zeta}\dfrac{H^m{}_{n-2}}{P^m{}_{n-2}}\cdot\dfrac{d}{d\zeta}\dfrac{H_n{}^m}{P_n{}^m}}\right\}_{\zeta=\zeta_0}-\beta_n{}^mE_{n+2,\,m}\left\{\frac{\dfrac{d}{d\zeta}\dfrac{Q^m{}_{n+2}}{P^m{}_{n+2}}\cdot\dfrac{d}{d\zeta}\dfrac{H^m{}_{n+2}}{P_n{}^m}}{\dfrac{d}{d\zeta}\dfrac{H^m{}_{n+2}}{P^m{}_{n+2}}\cdot\dfrac{d}{d\zeta}\dfrac{H_n{}^m}{P_n{}^m}}\right\}_{\zeta=\zeta_0}$$
$$+\text{relative } O(k^4), \qquad B_{nm}=\text{relative } O(k^4). \quad (18)$$

In order to simplify the formulae somewhat we will specify that the charge ϵz_1 is located on the z axis at a distance ρ from the origin, so that $\cosh\eta'=\rho/c$, $\cos\vartheta'=1$ or $\cosh\eta'=1$, $\cos\vartheta'=\rho/c$, according to whether $\rho>c$ or $\rho<c$. There is no significant loss in generality in this restriction since we are mainly interested in the extreme case of a long thin ion in which the charge could not be far removed from the major axis. In this case the potentials are independent of the coordinate φ, so that m is to be set equal to zero in all the above formulae.

Now if $c\leq3\times10^{-8}$ cm and we restrict ourselves to the consideration of solutions in which $\mu^{\frac{1}{2}}\leq0.1$ we may write that

$$H^{(1)}{}_{n+\frac{1}{2}}(ik\zeta)\approx\frac{1\cdot3\cdot5\cdots(2n-1)}{i^{n+\frac{1}{2}}}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}(k\zeta)^{-n-\frac{1}{2}}, \qquad H_{\frac{1}{2}}{}^{(1)}(ik\zeta)\approx\frac{1}{i^{\frac{1}{2}}}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\frac{1-k\zeta}{(k\zeta)^{\frac{1}{2}}},$$
$$a_{n,\,2j}\approx k^{2j}\frac{(n+1)(n+2)\cdots(n+2j)}{2\cdot4\cdots(2j)(2n+1)(2n+3)^2(2n+5)^2\cdots(2n+2j+1)^2(2n+2j+3)\cdots(2n+4j-1)}. \quad (19)$$

The relative error in these approximations is less than 0.5 percent if $\zeta<1.2$. We thus obtain the simple result that

$$H_n(\zeta)=k^{-n-1}Q_n(\zeta), \qquad H_0(\zeta)=-1+k^{-1}Q_0(\zeta), \quad (20)$$

so that the expression for $\psi_2(\zeta_0,\vartheta)$, omitting certain negligible terms, is

$$\psi_2(\zeta_0,\vartheta)=-\frac{\epsilon z_1\kappa}{D}+\frac{\epsilon z_1}{D}\sum_{n=0}^{\infty}\left\{(2n+1)P_n\left(\frac{\rho}{c}\right)Q_n(\zeta_0)\right.$$
$$+\frac{k^2}{2}\frac{n(n-1)}{(2n-1)^2}P_{n-2}\left(\frac{\rho}{c}\right)\left[Q_{n-2}+(\zeta^2-1)(P_n)^2Q_n\frac{d}{d\zeta}\frac{Q_{n-2}}{P_n}\right]_{\zeta=\zeta_0}$$
$$\left.-\frac{k^2}{2}\frac{(n+1)(n+2)}{(2n+3)^2}P_{n+2}\left(\frac{\rho}{c}\right)\left[Q_{n+2}+(\zeta^2-1)(P_n)^2Q_n\frac{d}{d\zeta}\frac{Q_{n+2}}{P_n}\right]_{\zeta=\zeta_0}\right\}P_n(\cos\vartheta). \quad (21)$$

It can be shown by using the asymptotic values

$$Q_n(\zeta) \approx \left(\frac{\pi}{n}\right)^{\frac{1}{2}} \frac{e^{-(n+\frac{1}{2})\eta}}{(2 \sinh \eta)^{\frac{1}{2}}},$$

$$P_n(\zeta) \approx \frac{1}{(n\pi)^{\frac{1}{2}}} \frac{e^{(n+\frac{1}{2})\eta}}{(2 \sinh \eta)^{\frac{1}{2}}}, \quad n \gg 1$$

valid for $\zeta = \cosh \eta > 1$, that the relative error introduced into each term of the sum in (21) by omitting the k^2 terms vanishes with increasing n. Moreover these errors are certainly monotonic functions of n for values of ζ_0 and ρ/c sufficiently near unity and for n greater than 5 or 6. We can thus obtain an estimate of the total error involved in neglecting these terms by examining the first few. Taking $\zeta_0 = 1.1$ and $\rho/c = 1.05$, we find that the error is certainly considerably less than 1 percent. This value of ζ_0 corresponds to an ion having a major axis about $2\frac{1}{2}$ times as long as its minor axis. Thus even in quite extreme cases we may write with sufficient accuracy,

$$\psi_2(\zeta_0, \vartheta) = -\epsilon z_1 \kappa/D + (\epsilon z_1/D) \sum_{n=0}^{\infty} (2n+1) \times P_n(\rho/c) Q_n(\zeta_0) P_n(\cos \vartheta); \quad (22)$$

the first term is the potential due to the ionic atmosphere and the second term is that due to the charge ϵz_1, so that we obtain again the simple Debye-Hückel result.

To evaluate the orientation factor Ω appearing in Eq. (2) we assume that the irreversible chemical reaction between an ion of type 1 and one of type 2 (the latter being spherically symmetrical) can take place only when the charge of the ion 2 is located on the spheroid defined by $\eta = \eta_0$, and the line joining the centers of the ions is contained within a solid angle $\Delta\omega$ determined by the finite reactive portion of the surface of the ion 1. This picture should serve as a simplified representation of a reaction between a comparatively simple inorganic ion and a complicated organic ion, the reaction involving one particular group present in the latter. Then Ω is the fraction of the ions of type 2 with charges located on the spheroid which have the orientation necessary for reaction. If we assume a Boltzmann distribution[7] we have

$$\Omega(\eta_0) = \frac{\int_{\vartheta'}^{\vartheta''} \int_{\varphi'}^{\varphi''} \exp(-\epsilon z_2 \psi_2/kT) dS}{\int_0^{\pi} \int_0^{2\pi} \exp(-\epsilon z_2 \psi_2/kT) dS}, \quad (23)$$

where the limits ϑ', ϑ'', φ', φ'', correspond to $\Delta\omega$, dS is the element of surface, and k is Boltzmann's constant.

It is at once apparent that a potential of the form of (22) will lead to an Ω which is independent of κ. Furthermore, if we use ψ_2 in place of φ_1 in Eq. (2) we obtain, after introducing appropriate numerical values,

$$d \log k''/d(\mu)^{\frac{1}{2}} = z_1 z_2, \quad (24)$$

again in agreement with Brönsted's formula.

As might be expected, exactly the same result is obtained in the consideration of the simpler case of a spherical ion whose charge is not located at its center. It seems quite safe to draw the conclusion that no reasonable type of dissymmetry could lead to purely electrostatic orientation effects that would be observable at concentrations within the range where the Debye-Hückel theory may be applied with any degree of confidence. The observations of LaMer and Kamner[1] on the β-brompropionate-thiosulfate reaction can only be reconciled with the theory of Brönsted by assuming that the log k'' *vs.* $\mu^{\frac{1}{2}}$ curve has a maximum just below the last experimental point.

In conclusion, it is a pleasure for the author to express his gratitude to Professor Lars Onsager for many helpful suggestions given in connection with the treatment of the differential equations in this paper.

[7] See Christiansen, reference 2, p. 43.

Statistical Mechanics of Fluid Mixtures*

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Expressions for the chemical potentials of the components of gas mixtures and liquid solutions are obtained in terms of relatively simple integrals in the configuration spaces of molecular pairs. The molecular pair distribution functions appearing in these integrals are investigated in some detail, in their dependence upon the composition and density of the fluid. The equation of state of a real gas mixture is discussed, and an approximate molecular pair distribution function, typical of dense fluids, is calculated. Applications of the method to the theory of solutions will be the subject of a later article.

I.

ALTHOUGH statistical mechanics has met with considerable success in the interpretation of the properties of rarefied gases as well as those of crystalline solids, serious practical difficulties have retarded its application to dense gases and to liquids. In the present article, we shall describe a statistical treatment of fluid mixtures, which is formally applicable both to real gases and to liquids. It has the advantage of yielding expressions which lend themselves more readily than the usual statistical formulas, to approximations suitable for condensed systems. While we make no pretension to a resolution of the difficulties presented by the liquid state, the more serious of which resist more than a superficial treatment, we believe that the method to be described throws interesting light upon the problem, and that it may prove useful in opening up new lines of attack, particularly in the field of liquid solutions.

We must first ask whether classical statistical mechanics is competent to describe the dependence of the thermodynamic functions of fluids upon intermolecular forces. At ordinary temperatures, there is good reason to believe that the classical approximation is adequate for most gases and liquids consisting of chemically saturated molecules. When certain conditions involving the molecular masses, moments of inertia, and the intermolecular forces are satisfied, the partition function of a system of molecules is closely approximated by the product of a function of the temperature alone, and the Gibbs phase integral in the phase space associated with the low frequency translational and rotational motion of the molecules.[1] The validity of the assumptions involved in this approximation is of course more questionable for liquids than for gases, particularly when there is strong coupling between the rotational motion of neighboring molecules as in polar liquids. We shall provisionally assume the adequacy of the classical approximation, remembering that our results are applicable only when this is true.

When the potential of the intermolecular force is of special form, for example a sum of terms depending upon the relative coordinates of molecular pairs, the explicit use of unwieldy integrals in a many dimensional phase space may be avoided. We shall show how the statistical formulas for certain important thermodynamic functions of a fluid mixture may be recast in terms of comparatively simple integrals in the configuration space associated with the relative motion of a molecular pair. The molecular pair distribution functions, which appear in these integrals are, to be sure, formally defined as ratios of many dimensional phase integrals. However, by certain transformations, they may be expressed in a form which leads to reasonable approximations both in condensed and rarefied systems. The approximation for rarefied systems leads to a novel approach to the problem of the equation of state of a real gas, while the approximation for condensed system promises to be of use in the theory of liquid solutions. On the other hand, the approximate distribution functions which have thus far been obtained do not

* The material of Section V of this article was presented at the eighty-ninth meeting of the American Chemical Society held in New York City during the week of April 22, 1935.

[1] E. Wigner, Phys. Rev. **40**, 749 (1932); Uhlenbeck and Gropper, Phys. Rev. **41**, 79 (1932); J. G. Kirkwood, Phys. Rev. **44**, 31 (1933); J. Chem. Phys. **1**, 597 (1933).

appear to be sufficiently exact for the calculation of the equations of state of liquids.

The method of the present treatment is based upon the same principle as the charging processes employed in the theory of electrolyte solutions. As Onsager has clearly pointed out, parameters which appear in the potential of the intermolecular forces have essentially the same status as the parameters of external force,[2] which determine the mechanical interaction between a thermodynamic system and its surroundings, and may be manipulated in the same manner. The application of this principle is by no means restricted to intermolecular forces of the Coulomb type, in the potential of which ionic charges enter as natural parameters. Arbitrary parameters may be introduced into the potential of intermolecular force in any system of molecules, by means of which the coupling between the molecules may be continuously varied in any convenient manner. This device allows one to express the chemical potential of any component of a fluid mixture in a particularly simple form. It also proves to be very useful in investigating the dependence of molecular pair distribution functions upon the composition and density of the fluid.

II.

The following analysis is formally applicable to all homogeneous fluids, whether real gas mixtures or liquid solutions. Differences arise only in the method of approximating distribution functions. We therefore consider a homogeneous fluid of ν substances, in thermodynamic equilibrium. By suitably restricting the ranges of composition and pressure so as to exclude coexistent phases containing any of its components, we may suppose that the fluid completely fills a vessel of volume v, which confines the motion of the system to a finite region of configuration space.[3] We denote the absolute temperature by T, the numbers of molecules of the several components by $N_1, \cdots, N_\nu$, and the total number of molecules of all species, $\sum_{s=1}^{\nu} N_s$, by N. According to classical statistical mechanics, we represent the system by a canonically distributed petit ensemble, and obtain the usual expression for the Helmholtz free energy, F_N.

$$e^{-\beta F_N} = \left[\prod_{s=1}^{\nu} \frac{f_s(T)^{N_s}}{N_s!}\right] Z_N$$

$$Z_N = \int \cdots \int e^{-\beta V_N} d\omega_1 \cdots d\omega_N, \qquad (1)$$

where β is equal to $1/kT$ and $d\omega_i$ is a differential element of the configuration space associated with the low frequency rotational and translational degrees of freedom of the molecule i. The integration in the sub-space of each molecule is extended over a region bounded by the volume of the vessel containing the fluid. In general

$$\int d\omega_i = \sigma_i v \qquad (2)$$

where σ_i is equal to 4π for diatomic molecules which have only two low frequency rotational degrees of freedom and to $8\pi^2$ for polyatomic molecules which in general have three. The potential of the intermolecular forces, V_N, is a function of the configuration coordinates of all N molecules. The functions $f_s(T)$, depending upon the temperature alone, are products of certain momentum integrals associated with the low frequency degrees of freedom of a molecule of type s and the partition function associated with its high frequency vibrational degrees of freedom. For our present purposes we do not need to characterize these functions more closely.

The chemical potential per molecule of a component i of the fluid is thermodynamically defined by the relation

$$\mu_i = (\partial F/\partial N_i)_{T,\, v,\, N_1,\, \ldots N_{\nu-1}}. \qquad (3)$$

It is statistically defined by Gibbs[4] in terms of the grand ensemble. For our purposes, it is more convenient to define μ_i in terms of the petit ensemble upon which Eq. (1) is based. This may

[2] L. Onsager, Chem. Rev. **13**, 73 (1933); J. W. Gibbs, *Elementary Principles in Statistical Mechanics, Collected Works II*, Chap. VII (Longmans).

[3] We postulate the absence of coexistent phases containing any of the components of the fluid, since we wish to represent the system by a petit ensemble, each example of which contains the same number of molecules. Actually this is a trivial restriction, for Gibbs has shown that although an open system is represented by a grand ensemble, its equilibrium properties do not differ sensibly from those of a closed system represented by a petit ensemble, each example of which is made up of the average number of molecules of a system of the grand ensemble. In case coexistent phases exist, we simply regard v as the volume of the homogeneous part in which we are interested.

[4] J. W. Gibbs, *Elementary Principles in Statistical Mechanics, Collected Works II*, p. 187, Longmans.

be done in a very simple manner. We first observe that the treatment of N as a continuous variable in the thermodynamic definition (3) is simply a convenient mathematical device. A physical definition of chemical potential requires the use of finite differences, ΔF and ΔN_i, in the ratio $\Delta F/\Delta N_i$. For values of ΔN_i which do not sensibly affect the composition of the fluid, this ratio will not differ sensibly from the derivative on the right-hand side of Eq. (3). We are therefore justified in defining μ_i as the change in free energy produced by the subtraction or addition of a single molecule of type i from the macroscopic system, while maintaining the temperature, volume and the numbers of molecules of the other species constant.

$$\mu_i = F(N_1, \cdots, N_i, \cdots N_\nu, T, v) - F(N_1, \cdots, N_i - 1, \cdots N_\nu, T, v). \quad (4)$$

The fact that the removal of a single molecule is scarcely a physically realizable process does not alter the value of the definition (4) when used in conjunction with the petit ensemble, each system of which is supposed to comprise exactly the same number of molecules.

From Eqs. (1) and (4), we obtain the following expression for μ_i:

$$\mu_i = -kT \log\left[\frac{f_i(T)}{N_i}\frac{Z(N_1, \cdots, N_i, \cdots N_\nu, T, v)}{Z(N_1, \cdots, N_i - 1, \cdots N_\nu, T, v)}\right]. \quad (5)$$

Further simplification depends upon the form of the potential of the intermolecular forces, V_N. We shall treat here only systems, for which V_N may be expressed as a sum of terms V_{kl}, each depending only upon the relative coordinates of a molecular pair (kl).[5]

$$V_N = \sum_{k<l} V_{kl}. \quad (6)$$

We now define a fictitious potential of the following type

$$V_N(\lambda_1, \cdots \lambda_N) = \sum_{k<l} \lambda_k \lambda_l V_{kl}, \quad (7)$$

where $\lambda_1 \cdots \lambda_N$ are arbitrary parameters. By varying these parameters between zero and unity, we can continuously vary the coupling between the N molecules from zero to its full value. In particular, we notice that when a value unity is assigned to each of the N parameters λ, we have

$$V_N(1, \cdots, 1) = V_N, \quad (8)$$

where V_N is given by Eq. (6) and represents the actual coupling between the molecules. If, on the other hand, a value unity is assigned to $N-1$ of the parameters λ and a value zero to a single λ_i, we have

$$V_N(1, \cdots, 0, \cdots 1) = V_{N-1}, \quad (9)$$

where V_{N-1} is the potential in a system of $N-1$ molecules formed by the removal of a single molecule i. Corresponding to $V_N(\lambda_1, \cdots \lambda_N)$, we define a phase integral,

$$Z_N(\lambda_1, \cdots \lambda_N) = \int \cdots \int e^{-\beta V_N(\lambda_1 \cdots \lambda_N)} d\omega_1 \cdots d\omega_N. \quad (10)$$

When each of the parameters, λ, is assigned the value unity, we have the following identity:

$$Z_N(1, \cdots 1) = Z(N_1, \cdots, N_i, \cdots N_\nu). \quad (11)$$

When $N-1$ of the parameters λ are equal to unity, while a single λ_i corresponding, let us say,

[5] It is to be remarked that the potential of Eq. (6) in no way excludes the simultaneous interaction of groups of more than two molecules. It simply states that in such a group, the mutual potential energy of any pair is independent of the presence of the other molecules. For example the electrostatic energy of a system of point charges is of this type. London has shown that the potential of the attractive van der Waals forces between chemically saturated molecules satisfies the requirements of Eq. (6). [F. London, Zeits. f. physik. Chemie **11**, 222 (1930).]

No such clear cut statement can be made regarding the repulsive forces, which operate at small distances, determining the effective collision diameters of molecules. However, it is plausible to assume that the potentials of these forces are approximately additive, and even if they are not exactly so, it is only necessary for our purposes that their narrow range of action is not sensibly displaced. In general, we should expect terms depending upon the relative coordinates of three or more molecules to be important only if the total intermolecular field is strong enough to produce a large perturbation in the electronic structure of a molecule in the fluid. Theoretical considerations suggest that not only in gases but also in liquids, this is not the case. Empirical arguments against any appreciable distortion of the electronic structure of molecules in most liquids are furnished by spectroscopic and optical evidence. For example, the molecular refractivity of most liquids is substantially the same as that of their vapor.

There are to be sure some types of intermolecular potential which do not satisfy Eq. (6), for example those of chemical forces of the homeopolar type. Another example is furnished by the energy of polarization of a molecule by a group of ions.

to a molecule of type i is equal to zero, we may write

$$Z_N(1, \cdots, 0, \cdots 1) = \int \cdots \int e^{-\beta V_{N-1}} d\omega_1 \cdots d\omega_N. \quad (12)$$

Now since V_{N-1} contains no terms depending upon the coordinates of the molecule i, the integration over its configuration space in Eq. (12) may be carried out immediately. Performing this integration and making use of Eqs. (1) and (2), we obtain

$$Z_N(1, \cdots, 0, \cdots 1) = \sigma_i v Z(N_1, \cdots, N_i - 1, \cdots N_\nu). \quad (13)$$

From Eqs. (11) and (13) we may write

$$\frac{Z(N_1, \cdots, N_i, \cdots N_\nu)}{Z(N_1, \cdots, N_i - 1, \cdots N_\nu)} = \sigma_i v \frac{Z_N(1, \cdots, 1, \cdots 1)}{Z_N(1, \cdots, 0, \cdots 1)}. \quad (14)$$

Further we have the identity,

$$\log \frac{Z_N(1, \cdots, 1, \cdots 1)}{Z_N(1, \cdots, 0, \cdots 1)} = \int_0^1 \frac{\partial \log Z_N(\lambda_i)}{\partial \lambda_i} d\lambda_i. \quad (15)$$

To simplify notation, we write $Z_N(\lambda_i)$ for $Z_N(1, \cdots, \lambda_i, \cdots 1)$. In the future this convention will be adopted for all functions of the parameters λ, only those differing from unity being explicitly indicated. Returning to Eq. (10), we observe that

$$Z_N(\lambda_i) = \int \cdots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_N, \quad (16)$$

$$V_i = \sum_{k=1}^{N} V_{ik}.$$

Differentiation of (16) with respect to λ_i yields

$$\partial \log Z_N(\lambda_i)/\partial \lambda_i = -\beta \overline{V_i(\lambda_i)},$$

$$\overline{V_i(\lambda_i)} = \frac{\int \cdots \int V_i e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_N}{\int \cdots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_N}. \quad (17)$$

Combining Eqs. (5), (14), (15) and (17), we obtain for the chemical potential:

$$\mu_i = kT \log N_i/v + \int_0^1 \overline{V_i(\lambda_i)} d\lambda_i + \varphi_i(T), \quad (18)$$

$$\varphi_i(T) = -kT \log \sigma_i f_i(T).$$

The mean potential energy $\overline{V_i(\lambda_i)}$ can be expressed as follows:

$$\overline{V_i(\lambda_i)} = \sum_{k=1}^{N} \overline{V_{ik}(\lambda_i)},$$

$$\overline{V_{ik}(\lambda_i)} = \frac{\int \cdots \int V_{ik} e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_N}{\int \cdots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_N}. \quad (19)$$

Since V_{ik} depends only on the coordinates of the molecules i and k, we may write,

$$\overline{V_{ik}(\lambda_i)} = \frac{1}{\sigma_i \sigma_k v^2} \int \int V_{ik} e^{-\beta W_i^k(\lambda_i)} d\omega_i d\omega_k, \quad (a)$$

(20)

$$e^{-\beta W_i^k(\lambda_i)} = \frac{\sigma_i \sigma_k v^2 \int \cdots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_{N-2}}{\int \cdots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \cdots d\omega_N}. \quad (b)$$

The function $W_i^k(\lambda_i)$, as we shall presently show, is the potential of the mean force acting between the molecules i and k. At present we merely observe that in the absence of external fields of force $W_i^k(\lambda_i)$ can depend only upon the relative coordinate of the molecule pair i and k, except in a region of negligible volume near the surface of the fluid.

We may therefore refer the position of the center of gravity and the orientation of the molecule k to a coordinate system fixed in molecule i. Both V_{ik} and $W_i^k(\lambda_i)$ will depend upon these relative coordinates alone. Moreover, the Jacobian of this transformation is unity. If we then integrate over the configuration space of molecule i, the expression for $\overline{V_{ik}(\lambda_i)}$, Eq. (20), becomes:

$$\overline{V_{ik}(\lambda_i)} = (1/\sigma_k v) \int V_{ik} e^{-\beta W_i^k(\lambda_i)} d\omega_k, \quad (21)$$

where $d\omega_k$ is understood to refer to the coordinates of molecule k relative to a system of axes fixed in molecule i. Introducing Eq. (21) into Eq. (18), and remembering that $\overline{V_{ik}(\lambda_i)}$

is the same function for all molecules k of the same type, we may write:

$$\mu_i = kT\left\{ \log N_i/v + \sum_{k=1}^{\nu} \frac{N_k}{v}\int_0^1 B_{ik}(\lambda_i)d\lambda_i \right\} + \varphi_i(T), \tag{22}$$

$$B_{ik}(\lambda_i) = (1/\sigma_k kT)\int V_{ik}e^{-\beta W_i^k(\lambda_i)}d\omega_k,$$

where the summation extends over all molecular types k present in the fluid, and the function B_{ik} refers to a single pair of molecules of types i and k, respectively. Each B_{ik} is a function of temperature, volume and composition, since $W_i^k(\lambda_i)$ is a function of all of these variables. The notation $W_i^k(\lambda_i)$ means of course that all the parameters λ have the value unity except λ_i corresponding to a *single* molecule of type i.

The mean energy $\bar{E}$ of the fluid may be expressed quite simply, if we assume classical equipartition with respect to the low frequency rotational and translational degrees of freedom

$$\bar{E} = E_0(T) + \bar{V}_N, \tag{23}$$

where $\bar{V}_N$ is the mean potential energy associated with the intermolecular forces and $E_0(T)$, a function of the temperature alone, is sum of the internal energies of the molecules and their mean translational and rotational kinetic energies. Writing V_N in the form of Eq. (6), and remembering that V_{ik} depends only on the relative coordinates of molecules k and i, we may write*

$$\bar{V}_N = \sum_{i<k} \bar{V}_{ik} = \tfrac{1}{2}\sum_{\substack{i,k\\=1}}^{\nu} (N_iN_k/v)\,\bar{V}_{ik},$$

$$\bar{V}_{ik} = (1/\sigma_k v)\int V_{ik}e^{-\beta W_i^k(1)}d\omega_k. \tag{24}$$

We note that W_i^k appearing in Eq. (24) is $W_i^k(1)$, the value of $W_i^k(\lambda_i)$ when molecule i has its full coupling with the other molecules of the system. Finally we may write,

$$\bar{E} = E_0(T) + \tfrac{1}{2}kT\sum_{\substack{i,k\\=1}}^{\nu} (N_iN_k/v)B_{ik}. \tag{25}$$

The quantity B_{ik} in Eq. (25) is equal to $B_{ik}(1)$ of Eq. (22) when λ_i is unity. $E_0(T)$ may be explicitly calculated if the internal partition functions of the molecules are known. We shall not be interested in this point here.

III.

The use of Eqs. (22) and (25) for purposes of calculation depends upon an investigation of the functions $W_i^k(\lambda_i)$ which determine the probability distribution of the pair of molecules i and k relative to each other. It may readily be shown that $W_i^k(\lambda_i)$ is the potential of the mean force acting between the molecules i and k, averaged over all configurations of the remaining $N-2$ molecules of the system. The force acting at the center of gravity of molecule i for a fixed configuration of the other molecules, is

$$F_i(\lambda_i) = -\nabla_i V_N(\lambda_i), \tag{26}$$

where ∇_i is the gradient operator associated with the coordinates of the center of gravity of molecule i. If we take a mean value with the pair of molecules i and k held fixed, we obtain

$$\overline{F_i(\lambda_i)}^{ik} = -\frac{\int\cdots\int \nabla_i V_N(\lambda_i)e^{-\beta V_N(\lambda_i)}d\omega_1\cdots d\omega_{N-2}}{\int\cdots\int e^{-\beta V_N(\lambda_i)}d\omega_1\cdots d\omega_{N-2}}. \tag{27}$$

Differentiation of both sides of Eq. (20b), which defines $W_i^k(\lambda_i)$ and comparison with Eq. (27) yields

$$\overline{F_i(\lambda_i)}^{ik} = -\nabla_i W_i^k(\lambda_i). \tag{28}$$

The function $W_i^k(\lambda_i)$ is therefore the potential of the mean force acting at the center of gravity of molecule i when k is held fixed at some point in its vicinity. Similarly, it may be shown that $W_i^k(\lambda_i)$ is the potential of the mean generalized forces associated with the relative orientation of i and k. If the relative orientation is specified by the Eulerian angles ϑ, φ and ψ, the mean torque tending to produce rotation through the angle ϑ is $-\partial W_i^k(\lambda_i)/\partial\vartheta$. These relations have been used by Einstein, Schmoluchowski and others,[6] who showed that the simple Boltzmann distribution is valid provided the potential of the mean force is employed in the exponential factor.

It is interesting to remark that the potential $W_i^k(1)$, corresponding to full coupling between molecule i and the other molecules, is susceptible

* Eq. (24) has been given by Hildebrand and Wood, J. Chem. Phys. **1**, 817 (1933).

[6] For a discussion of this point, see L. Onsager, Chem. Rev. **13**, 73 (1933).

of experimental determination, at least in its dependence on the relative coordinates of the molecular centers of gravity. According to the theory of x-ray scattering by liquids, developed by Prins and Debye,[7] the angular distribution of intensity of the scattered radiation is a sum of mean values of functions depending only upon the relative coordinates of pairs of molecules. Mean values of such functions are determined by the probability distribution function $e^{-\beta W_i{}^k}$ in a system in thermodynamic equilibrium. By a Fourier integral inversion of the theoretical scattering formula, $(e^{-\beta W_i{}^k}-1)$ may be computed from the observed intensity measured as a function of the scattering angle. By Eq. (25), we see that a knowledge of $W_i{}^k(1)$ suffices for the calculation of the mean energy of the fluid from the potentials V_{ik}. However, it does not suffice for the calculations of chemical potentials or the Gibbs free energy, ζ, which is equal to $\sum_{i=1}^{\nu} N_i\mu_i$. For the latter purpose we must know $W_i{}^k(\lambda_i)$ for all values of λ_i between zero and unity. This information is not furnished by x-ray scattering experiments. Thus, while they yield valuable information concerning the statistical structure of liquids, they do not provide sufficient data for the calculation of entropy and free energy.

We must consequently depend upon theoretical information about the potentials of mean force $W_i{}^k(\lambda_i)$. Since the many dimensional phase integrals of Eq. (20b), which defines $W_i{}^k(\lambda_i)$, are inconvenient to handle, we follow an indirect method of attack, leading to reasonable approximations both for condensed and rarefied systems. Logarithmic differentiation of both sides of Eq. (20b) yields

$$\partial W_i{}^k(\lambda_i)/\partial\lambda_i = \overline{{}^{ik}V_i(\lambda_i)} - \overline{V_i(\lambda_i)}, \qquad (29)$$

where

$$\overline{{}^{ik}V_i(\lambda_i)} = \frac{\int\cdots\int V_i e^{-\beta[V_{N-1}+\lambda_i V_i]}d\omega_1\cdots d\omega_{N-2}}{\int\cdots\int e^{-\beta[V_{N-1}+\lambda_i V_i]}d\omega_1\cdots d\omega_{N-2}}, \qquad (30)$$

$\overline{{}^{ik}V_i(\lambda_i)}$ is the mean value of V_i for a fixed configuration of the molecular pair i and k, while $\overline{V_i(\lambda_i)}$ is the mean value of the same function taken over all configurations of all molecules of the system. By Eq. (10), we may write

$$\overline{{}^{ik}V_i(\lambda_i)} = V_{ik} + \sum_{\substack{s=1\\ \neq k}}^{N} \overline{{}^{ik}V_{is}(\lambda_i)}, \qquad (31)$$

since the term V_{ik} is constant for fixed configurations of molecules i and k and is unaffected by a mean value operation in which these are held fixed. Because V_{is} depends only on the relative coordinates of i and s, we have

$$\overline{{}^{ik}V_{is}(\lambda_i)} = (1/\sigma_s v)\int V_{is}e^{-\beta W_{ik^s}(\lambda_i)}d\omega_s, \qquad (32a)$$

$$e^{-\beta W_{ik^s}(\lambda_i)} = \frac{\sigma_s v\int\cdots\int e^{-\beta[V_{N-1}+\lambda_i V_i]}d\omega_1\cdots d\omega_{N-3}}{\int\cdots\int e^{-\beta[V_{N-1}+\lambda_i V_i]}d\omega_1\cdots d\omega_{N-2}}, \qquad (32b)$$

where the integration in the numerator of (32b) is to extend over the coordinates of all molecules except i, k and s and in the denominator over all but those of i and k. It will be seen at once that $W_{ik^s}(\lambda_i)$ is the potential of the mean force acting upon molecule s, averaged over the configurations of all molecules except i, k and s. We note that $W_{ik^s}(\lambda_i)$ is not invariant under a permutation of upper and lower indices, although $W_i{}^k(\lambda_i)$ is. It is possible to define a potential of mean force which is symmetric in the coordinates of i, k and s, differing from $W_{ik^s}(\lambda_i)$ by a term independent of the coordinates of s, but the latter form is not the most convenient for the present purposes. The second term of Eq. (29) is the sum $\sum_{s=1}^{N}\overline{V_{is}(\lambda_i)}$, each member of which is given by an expression of the form (21). Moreover, each of the mean values ${}^{ik}\bar{V}_{is}$ and $\bar{V}_{is}$ are identical molecules of the same type s, so that we may write,

$$\partial W_i{}^k(\lambda_i)/\partial\lambda_i = V_{ik} + \sum_{s=1}^{\nu}\frac{N_s}{v}\frac{1}{\sigma_s}\int V_{is}[e^{-\beta W_{ik^s}(\lambda_i)} - e^{-\beta W_i{}^s(\lambda_i)}]d\omega_s, \qquad (33)$$

where the sum is extended over all types s. Each of the integrals refers to a single group of three molecules, i, k, and a single molecule of type s. Properly a term, $(v\sigma_k)^{-1}\int V_{ik'}e^{-\beta W^{k'}{}_{ik}(\lambda_i)}d\omega_{k'}$, where k' is a single molecule of the same type as k, should be omitted from the sum in Eq. (33). Since, however, this term bears a ratio of the

[7] Zernicke and Prins, Zeits. f. Physik **41**, 184 (1927); Debye and Mencke, Physik. Zeits. **31**, 797 (1930).

order of $1/N_k$ to terms retained, it can be ignored altogether. This is not true of V_{ik}, which is of dominant importance when k is situated in the immediate neighborhood of i.

Before integrating Eq. (33) we shall find it convenient to investigate the behavior of $W_i^k(\lambda_i)$ in the neighborhood of $\lambda_i=0$. First we note that $W_i^k(0)$ must be independent of the coordinates of i, since the mean force on i vanishes when λ_i is equal to zero. Moreover, it must also be independent of the coordinates of k except in the surface region, since the mean force on k must also vanish when λ_i is equal to zero. From these facts we conclude that $W_i^k(0)$ must be a constant. Making use of Eq. (20b), we write

$$e^{-\beta W_i^k(0)}=\frac{\sigma_i\sigma_k v^2\int\cdots\int e^{-\beta V_{N-1}}d\omega_1\cdots d\omega_{N-2}}{\int\cdots\int e^{-\beta V_N}d\omega_1\cdots d\omega_N}. \tag{34}$$

Now the integral in the denominator of (34) is obviously independent of the coordinate of i and k, since it includes integrations over these coordinates. Since $W_i^k(0)$ is independent of the coordinates of i and k, we must conclude that the integral in the numerator is also independent of them. The factor $\sigma_i\sigma_k v^2$ may therefore be written as an integration over the configuration spaces of molecules i and k,

$$\sigma_i\sigma_k v^2\int\cdots\int e^{-\beta V_{N-1}}d\omega_1\cdots d\omega_{N-2}=\int\cdots\int e^{-\beta V_N}d\omega_1\cdots d\omega_N. \tag{35}$$

From Eqs. (34) and (35) we conclude that $e^{-\beta W_i^k(0)}$ has the value unity and that $W_i^k(0)$ vanishes. Bearing this fact in mind, we integrate Eq. (33) between zero and λ_i with the result:

$$W_i^k(\lambda_i)=\lambda_i V_{ik}+\sum_{s=1}^{\nu}(N_s/v)(1/\sigma_s)\int_0^{\lambda_i}\int V_{is}[e^{-\beta W_{ik}^s(\lambda_i)}-e^{-\beta W_i^s(\lambda_i)}]d\omega_s d\lambda_i. \tag{36}$$

From Eq. (36), we observe that $W_i^k(\lambda_i)$ approaches $\lambda_i V_{ik}$ as the densities of the several components of the fluid approach zero. This approximation is also obtained by neglecting the influence of the fixed molecule k on the distribution of a third molecule s in the vicinity of molecule i, that is by ignoring the difference between $W_{ik}^s(\lambda_i)$ and $W_i^s(\lambda_i)$. In the theory of the equation of state of a rarefied gas, this is essentially the approximation which is made. To obtain a more accurate expression for $W_i^k(\lambda_i)$ we must know something about the potential $W_{ik}^s(\lambda_i)$ involving the group of three molecules i, k and s. Proceeding from Eq. (32b), which defines $W_{ik}^s(\lambda_i)$, we obtain by differentiation with respect to λ_i

$$\partial W_{ik}^s(\lambda_i)/\partial\lambda_i=\lambda_i V_{is}+\sum_{l=1}^{\nu}(N_l/v\sigma_l)\int V_{il}[e^{-\beta W_{iks}^l(\lambda_i)}-e^{-\beta W_{ik}^l(\lambda_i)}]d\omega_l, \tag{37}$$

$$e^{-\beta W_{iks}^l(\lambda_i)}=\frac{\sigma_l v\int\cdots\int e^{-\beta[V_{N-1}+\lambda_i V_{il}]}d\omega_1\cdots d\omega_{N-4}}{\int\cdots\int e^{-\beta[V_{N-1}+\lambda_i V_{il}]}d\omega_1\cdots d\omega_{N-3}}.$$

Examination of (32b) shows at once that $W_{ik}^s(0)$ is merely W_k^s in a system containing N_i-1 molecules of type i. It is apparent that this function can differ from W_k^s in the original system only by a quantity of completely negligible order, $O(1/N_i)$. Thus when Eq. (37) is integrated with respect to λ_i, there is obtained

$$W_{ik}^s(\lambda_i)=W_k^s+\lambda_i V_{is}+\sum_{l=1}^{\nu}(N_l/v\sigma_l)\int_0^{\lambda_i}\int V_{il}[e^{-\beta W_{iks}^l(\lambda_i)}-e^{-\beta W_{ik}^l(\lambda_i)}]d\omega_l d\lambda_i. \tag{38}$$

This equation is entirely analogous to Eq. (36). Since W_k^s is given by an equation of the form of (36), a first approximation to $W_{ik}^s(\lambda_i)$ is evidently $V_{ks}+\lambda_i V_{is}$. Similarly a first approximation to $W_i^s(\lambda_i)$ is $\lambda_i V_{is}$. If these approximations are employed in the integrals of Eq. (36), we obtain a second approximation to $W_i^k(\lambda_i)$, namely

$$W_i^k(\lambda_i)=\lambda_i V_{ik}-kT\sum_{s=1}^{\nu}(N_s/v)(1/\sigma_s)\int(e^{-\beta\lambda_i V_{is}}-1)(e^{-\beta V_{ks}}-1)d\omega_s. \tag{39}$$

We should expect this approximation to be adequate in gases of moderate density. The method of successive approximation employed to obtain Eq. (39), can of course be extended without great difficulty, by transforming the potentials $W_{iks}{}^{l}(\lambda_i)$, involving groups of four molecules, in exactly the same manner as $W_i{}^{k}(\lambda_i)$ and $W_{ik}{}^{s}(\lambda_i)$. Presumably any desired degree of approximation could be attained in this fashion, but the expressions become very cumbersome. It should also be remarked that the method of approximation just outlined can only be employed when no long range forces, such as the Coulomb forces, act between the molecules, for in such cases the integral of Eq. (39) diverges. It converges whenever the individual potentials decrease asymptotically at least as rapidly as $r_{ik}{}^{-4}$.

For an exact calculation of $W_i{}^{k}(\lambda_i)$, it would be necessary to solve a set of $N-1$ simultaneous integral equations of the type of Eqs. (36) and (38), involving potentials $W^{s}{}_{ik\cdots l}$, in which the number of fixed molecules $i, k, \cdots l$, ranges from one to $N-1$. Moreover, when the number of fixed molecules becomes comparable with the total number of molecules, N, the equations become more complicated than (36) and (38), due to growth of terms, which are of zero order in the latter equations. Since this is not a practicable procedure, we must resort to some means of approximation. Eq. (39) represents a possible method of approximation in which $W_i{}^{k}(\lambda_i)$ is developed in powers of the densities of the components of the fluid. However, we should like to find an approximation more suitable in condensed systems than Eq. (39) is likely to be. An obvious and simple approximation may be obtained by assuming superposition in the potentials of mean force,

$$W_{ik}{}^{s}(\lambda_i) = W_k{}^{s} + W_i{}^{s}(\lambda_i). \tag{40}$$

Although the additivity expressed in Eq. (40) holds for the direct action of i and k on s through the terms $V_{ks}+\lambda_i V_{is}$, it cannot hold exactly for their indirect action upon s through their effect on the distribution of the remaining $N-3$ molecules. The magnitude of this discrepancy will be discussed later. If we introduce the approximation (40) into Eq. (36), we obtain the following integral equation:

$$W_i{}^{k}(\lambda_i) = \lambda_i V_{ik} + \sum_{s=1}^{\nu} (N_s/v)(1/\sigma_s) \int_0^{\lambda_i} \int V_{is} e^{-\beta W_i{}^{s}(\lambda_i)} [e^{-\beta W_k{}^{s}(1)} - 1] d\omega_s d\lambda_i. \tag{41}$$

The potentials $W_i{}^{k}(\lambda_i)$ will have the same form for any pair of molecules of the same type. From the ν types of molecules present in the fluid, $\nu(\nu+1)/2$ types of molecular pairs can be formed. There will, therefore, be $\nu(\nu+1)/2$ types of functions $W_i{}^{k}(\lambda_i)$, each satisfying an equation like (41). Simultaneous solution of these integral equations will yield values of the functions $W_i{}^{k}(\lambda_i)$ consistent with the approximation expressed in Eq. (40). Of course for a pure fluid, having only one component, only one integral equation has to be solved.

$$W(q_{12}, \lambda) = \lambda V(q_{12}) + (N\rho/M\sigma) \int_0^{\lambda} \int V(q_{13}) e^{-\beta W(q_{13},\, \lambda)} [e^{-\beta W(q_{23},\, 1)} - 1] d\omega_3 d\lambda, \tag{42}$$

where q_{12}, q_{13} and q_{23} are the relative coordinates of a set of three molecules, N is Avogadro's number, M the molecular weight of the substance, and ρ its density. We note that the approximation (39) is obtainable from Eq. (41) as the first step in its solution by successive substitution. In general, it will not be feasible to seek analytic solutions of Eqs. (41) or (42). However, by graphical or mechanical quadrature, it should be possible to determine self-consistent functions satisfying these equations. We remark that this process provides a theoretical means of calculating the x-ray scattering curves of liquids, since they are determined by $W_i{}^{k}(1)$. In some cases the potentials of intermolecular force can be calculated from atomic structure. Although this can be done in relatively few cases, quantum mechanics prescribes an approximate functional form for the V_{ik}. With this functional form, the numerical values of V_{ik} may be deduced from the temperature dependence of the second virial coefficient of the substance in the gaseous state.

While Eq. (40) represents an approximation which is intuitively attractive, it is of course not exact. Although a numerical estimate of the error involved is difficult, we can say something quite

definite about the nature of the approximation. To facilitate discussion, we shall introduce the symbol ϵ_{ik^s} to denote the deviation from additivity

$$\epsilon_{ik^s} = W_{ik^s}(\lambda_i) - [W_{k^s} + W_{i^s}(\lambda_i)]. \tag{43}$$

It is possible to express ϵ_{ik^s} in terms of a third order fluctuation in the potential energy of molecule i. Without entering into the details of the calculation, we state the following result.

$$\epsilon_{ik^s} = \beta^2 \int_0^{\lambda_i} \int_0^1 \int_0^1 (V_t - \overline{V_{ik^s i}})(V_k - \overline{V_{ik^s k}})(V_s - \overline{V_{ik^s s}}) d\lambda_k d\lambda_s d\lambda_i, \tag{44}$$

where the fluctuation is understood to be a function of the variables λ_i, λ_k, λ_s, mean values being taken with the distribution function $e^{-\beta V_N(\lambda_i, \lambda_k, \lambda_s)}$. A more useful expression for ϵ_{ik^s} is obtained simply by subtracting the equation for $W_{i^s}(\lambda_i)$ corresponding to (36) from Eq. (38). The result is,

$$\epsilon_{ik^s} = \sum_{l=1}^{\nu} (N_l/v\sigma_l) \int_0^{\lambda_i} \int V_{il} \{ e^{-\beta W_{ik^s}{}^l(\lambda_i)} + e^{-\beta W_{i^s}{}^l(\lambda_i)} - e^{-\beta W_{ik}{}^l(\lambda_i)} - e^{-\beta W_{is}{}^l(\lambda_i)} \} d\omega_l d\lambda_i. \tag{45}$$

An exact calculation of ϵ_{ik^s} from Eq. (45) is of course impossible without a knowledge of the potential $W_{ik^s}{}^l(\lambda_i)$. However, we should expect to obtain at least a rough estimate of ϵ_{ik^s} by using the additivity approximation for the potentials $W_{ik^s}{}^l(\lambda_i)$, $W_{ik}{}^l(\lambda_i)$, and $W_{is}{}^l(\lambda_i)$. Introduction of this approximation yields

$$\epsilon_{ik^s} = \sum_{l=1}^{\nu} (N_l/v\sigma_l) \int_0^{\lambda_i} \int V_{il} e^{-\beta W_i{}^l(\lambda_i)} (e^{-\beta W_k{}^l} - 1)(e^{-\beta W_s{}^l} - 1) d\omega_l d\lambda_i. \tag{46}$$

If we rely on Eq. (46) for the order of magnitude of ϵ_{ik^s}, we see that the integrand will be very small except for configurations of molecule such that $W_k{}^l$ and $W_s{}^l$ are simultaneously large. If s and k are situated at some distance from each other so that their spheres of influence on the distribution of a third molecule l, do not overlap appreciably, ϵ_{ik^s} will be small. Returning to Eq. (36) we remark that for the calculation of $W_i{}^k(\lambda_i)$, it is only necessary to know $W_{ik^s}(\lambda_i)$ accurately in a region in the vicinity of molecule i, where V_{is} is sensibly different from zero. If the molecules i and k are separated by an appreciable distance, s will be distant from k in the greater part of this region, and we may conclude that ϵ_{ik^s} is small. Thus we may expect Eq. (41) to provide a good approximation to $W_i{}^k(\lambda_i)$ at least when the molecules i and k are separated by an appreciable distance, and that $W_i{}^k(\lambda_i)$ will approach the solution of Eq. (41) asymptotically as the distance between i and k is increased. This point is of some importance in the case of long range intermolecular forces, such as those between electrolyte ions. At small distances between i and k the dominant term in $W_i{}^k(\lambda_i)$ becomes V_{ik}, and although the terms depending on the density may still be large, it is not necessary to know them with such great accuracy. Once solutions of Eq. (41) have been obtained, they may be used in Eq. (46) to obtain a rough estimate of ϵ_{ik^s}. If this turns out to be small, the solutions of Eq. (41) can be accepted with some degree of assurance as reasonable approximations to the potentials $W_i{}^k(\lambda_i)$. It would be desirable to have a more rigid criterion for judging the adequacy of these approximations, but unfortunately this cannot be obtained without introducing distribution functions involving larger and larger groups of fixed molecules. Unless some approximation such as superposition is introduced at some early stage in this sequence of distribution functions, we are driven back to the many dimensional phase integrals with which we started.

Having obtained approximate expressions for $W_i{}^k(\lambda_i)$ by solution of Eqs. (41), we can calculate the chemical potential of any component of the fluid by means of Eq. (22), as well as the total energy of the fluid by Eq. (25). From the chemical potentials, we may obtain the Gibbs free energy, ζ, of the system.

$$\zeta = E + pv - TS = \sum_{i=1}^{\nu} N_i \mu_i = kT \left\{ \sum_{i=1}^{\nu} N_i \log N_i/v + \sum_{i,k=1}^{\nu} \frac{N_i N_k}{v} \int_0^1 B_{ik}(\lambda_i) d\lambda_i \right\} + \sum_{i=1}^{\nu} N_i \varphi_i(T). \tag{47}$$

In principle one can obtain the compressibility, κ, of the fluid by means of the thermodynamic formula,

$$1/\kappa = -v(\partial p/\partial v)_T = -(\partial \zeta/\partial v)_{T,\, N_1,\, \cdots N_\nu}. \tag{48}$$

However the $B_{ik}(\lambda_i)$ depend upon v through the $W_i^k(\lambda_i)$. Even though Eq. (41) may provide good approximations to the $W_i^k(\lambda_i)$, it is by no means certain that the derivatives of these solutions with respect to v will be good approximations to $\partial W_i^k(\lambda_i)/\partial v$. Thus while Eqs. (22), (35) and (47) may express the dependence of the μ_i, $\bar{E}$ and ζ upon the composition of the fluid with some accuracy, the compressibility calculated from Eqs. (47) and (48) may be a much poorer approximation. Quite formally, we may write

$$\left(\frac{\partial p}{\partial v}\right)_T = -kT\left\{\sum_{i=1}^{\nu}\frac{N_i}{v^2} + \sum_{i,\,k=1}^{\nu}\frac{N_iN_k}{v^3}\int_0^1\left[B_{ik}(\lambda_i) - v\frac{\partial B_{ik}(\lambda_i)}{\partial v}\right]d\lambda_i\right\}. \tag{49}$$

In case the fluid under consideration is a gas, we know that as the volume is increased to infinity, the pressure decreases continuously to zero. In this case we may integrate Eq. (49) between the limits v and infinity. After a simple partial integration, the following equation of state is obtained.

$$\frac{p\bar{v}}{RT} = 1 + \sum_{i,\,k=1}^{\nu}\frac{x_ix_k}{\bar{v}}\left\{\int_0^1 N\left[B_{ik}(\lambda_i) + \bar{v}^2\int_\infty^{\bar{v}}\frac{B_{ik}(\lambda_i)}{\bar{v}^3}d\bar{v}\right]d\lambda_i\right\} \tag{50}$$

$$n_i = N_i/N; \qquad x_i = n_i/\sum n_k; \qquad \bar{v} = v/\sum n_k,$$

where N is Avogadro's number, n_i the number of moles of component i present in the gas and x_i the mole fraction of that component. Eq. (50) may be made the basis for a statistical calculation of the equation of state of a real gas mixture. When the potentials $W_i^k(\lambda_i)$ in the $B_{ik}(\lambda_i)$ are approximated simply by $\lambda_i V_{ik}$ the usual expressions for the second virial coefficients are obtained.

IV.

The present method provides a particularly simple means of determining the equation of state of a real gas mixture. We shall derive expressions for the second and third coefficients in the virial expansion of the equation of state, indicating how the method may be extended to higher coefficients. Results are obtained which are in agreement with those of Ursell, who has treated the same problem from a somewhat different point of view.[8]

If the function $W_i^k(\lambda_i)$ is approximated by Eq. (39), we obtain the following expression for $B_{ik}(\lambda_i)$.

$$B_{ik}(\lambda_i) = \frac{1}{\sigma_k kT}\int V_{ik}\exp\left\{-\beta\lambda_i V_{ik} + \sum_{s=1}^{\nu}\frac{N_s}{v\sigma_s}\int(1-e^{-\beta\lambda_i V_{is}})(1-e^{-\beta V_{ks}})d\omega_s\right\}d\omega_k. \tag{51}$$

Substitution of this expression in Eqs. (22) and (50) would yield the chemical potentials of the several components and the equation of state of the gas mixture. We should expect the equation of state, although approximate, to be much more satisfactory than a virial expansion. However, the integrals involved cannot be expressed in terms of elementary functions, and we shall not concern ourselves with their simplification here. We note that Eq. (39) is exact to terms in $1/v^2$, so that the first two terms of an expansion of the right-hand side of Eq. (51) are exact. The expansion is

$$B_{ik}(\lambda_i) = \frac{1}{kT}\left\{\frac{1}{\sigma_k}\int V_{ik}e^{-\beta\lambda_i V_{ik}}d\omega_k + \sum_{s=1}^{\nu}\frac{N_s}{v}\frac{1}{\sigma_s\sigma_k}\int\int V_{ik}e^{-\beta\lambda_i V_{ik}}(1-e^{-\beta\lambda_i V_{is}})(1-e^{-\beta V_{ks}})d\omega_i d\omega_s + O(1/v^3)\right\}. \tag{52}$$

[8] Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927); R. H. Fowler, *Statistical Mechanics*, Cambridge University Press (1929), p. 173.

Substitution of this expansion in Eq. (22), integration with respect to λ_i and a rearrangement of terms yields[9]

$$\mu_i = kT\Big\{ \log N_i/v + \sum_{k=1}^{\nu} \frac{N_k}{v\sigma_k} \int (1-e^{-\beta V_{ik}}) d\omega_k + \tfrac{1}{2} \sum_{k,\,s=1}^{\nu} \frac{N_k N_s}{v^2} \frac{1}{\sigma_s \sigma_k} \int\int (1-e^{-\beta V_{ik}})(1-e^{-\beta V_{is}})(1-e^{-\beta V_{ks}}) d\omega_k d\omega_s + O(1/v^3) \Big\}. \quad (53)$$

When the approximate expressions for the μ_i given by Eq. (53) are introduced into Eqs. (47) and (48), we obtain

$$\left(\frac{\partial p}{\partial v}\right)_T = -kT\Big\{ \sum_{i=1}^{\nu} \frac{N_i}{v^2} + \sum_{i,\,k=1}^{\nu} \frac{N_i N_k}{v^3} \frac{1}{\sigma_k} \int (1-e^{-\beta V_{ik}}) d\omega_k + \sum_{i,\,k,\,s=1}^{\nu} \frac{N_i N_k N_s}{v^4} \frac{1}{\sigma_k \sigma_s} \int\int (1-e^{-\beta V_{ik}})(1-e^{-\beta V_{is}})(1-e^{-\beta V_{ks}}) d\omega_s d\omega_k + O(1/v^5) \Big\}. \quad (54)$$

Integration between the volume limits ∞ and v leads to the following equation of state

$$\frac{p\bar{v}}{RT} = 1 + \sum_{i,\,k=1}^{\nu} \frac{x_i x_k}{\bar{v}} B_{ik}{}^0 + \sum_{i,\,k,\,s=1}^{\nu} \frac{x_i x_k x_s}{\bar{v}^2} C_{iks}{}^0 + O(1/\bar{v}^3)$$

$$B_{ik}{}^0 = \frac{N}{2\sigma_k} \int (1-e^{-\beta V_{ik}}) d\omega_k \quad (55)$$

$$C_{iks}{}^0 = \frac{N^2}{3\sigma_k \sigma_s} \int\int (1-e^{-\beta V_{ik}})(1-e^{-\beta V_{is}})(1-e^{-\beta V_{ks}}) d\omega_k d\omega_s.$$

If the method of approximating $W_i{}^k(\lambda_i)$ embodied in Eq. (39) is carried one stage farther, one more term may be retained in the expansion of $B_{ik}(\lambda_i)$ and the fourth virial coefficient may be calculated. The process can be continued indefinitely, but of course the algebraic operations become tedious, and the final expressions unwieldy. The method consists simply of continued substitution and

[9] After integration with respect to λ_i, the terms in μ_i involving $1/v^2$ have the form

$$\sum_{\substack{k,\,s=1 \\ k\neq s\neq i}}^{N} \frac{1}{v^2 \sigma_k \sigma_s} \int\int (1-e^{-\beta V_{ks}}) \left\{ \frac{V_{ik}}{V_{ik}+V_{is}} (e^{-\beta(V_{ik}+V_{is})}-1) - (e^{-\beta V_{ik}}-1) \right\} d\omega_k d\omega_s,$$

where the original summation indices, referring to the individual molecules, have been restored for clearness. For every term in the sum with the integrand

$$\left\{ \frac{V_{ik}}{V_{ik}+V_{is}} (e^{-\beta(V_{ik}+V_{is})}-1) - (e^{-\beta V_{ik}}-1) \right\} (1-e^{-\beta V_{ks}}),$$

corresponding to any specified pair of molecules k and s, there is also a term involving the same pair, having the form

$$\left\{ \frac{V_{is}}{V_{is}+V_{ik}} (e^{-\beta(V_{ik}+V_{is})}-1) - (e^{-\beta V_{is}}-1) \right\} (1-e^{-\beta V_{ks}}).$$

The sum of this pair of terms is readily seen to be

$$(1-e^{-\beta V_{ik}})(1-e^{-\beta V_{is}})(1-e^{-\beta V_{ks}})$$

so that the double sum may be rearranged as follows:

$$\frac{1}{2} \sum_{\substack{k,\,s=1 \\ k\neq s\neq i}}^{N} \frac{1}{v^2 \sigma_k \sigma_s} \int\int (1-e^{-\beta V_{ks}})(1-e^{-\beta V_{is}})(1-e^{-\beta V_{ik}}) d\omega_k d\omega_s.$$

This sum contains $(N-1)(N-2)$ terms of similar magnitude. It differs from the sum over molecular types appearing in Eq. (55) by $(3N-2)$ terms of the same magnitude. The aggregate of these terms bears a ratio of the order of $1/N$ to either sum and is consequently entirely negligible.

expansion. If one wishes a virial expansion including terms of the order of $1/v^n$, one begins by approximating the $W^s{}_{ik\cdots l}$, involving n fixed molecules, by sums of the form $\lambda_i V_{is}+\sum_{l=1}^{n-1} V_{ls}$. These expressions, substituted in an equation similar to (38), yield an approximate $W^s{}_{ik\cdots l}$ involving $(n-1)$ fixed molecules. Continued substitution finally leads to an expression for $W_i{}^k(\lambda_i)$, which when expanded in powers of $1/v$, is exact to terms involving $1/v^n$. It is only necessary to have the expression for $W^s{}_{ik\cdots l}$ involving $(n-1)$ molecules, exact to terms in $1/v$, since in the final expansion, it is multiplied by a factor $1/v^{n-1}$.

V.

It is interesting to investigate the form of the molecular pair distribution function, $e^{-\beta W_i{}^k}$ by means of the approximation, Eq. (39). Although Eq. (39) can scarcely be accurate at liquid densities, we might expect it to be adequate up to moderately high densities. Moreover, even where inexact, it should serve to illustrate the form of the distribution function.

We shall restrict our attention to a pure fluid, consisting of spherically symmetrical molecules. For such a fluid, Eq. (39) reduces to the following expression when λ_i is equal to unity

$$W(r)=V(r)-(NkT/v)\times\int(1-e^{-\beta V(r_{13})})(1-e^{-\beta V(r_{23})})dv_3,$$

$$r=|\mathbf{r}_1-\mathbf{r}_2|\ ;\ r_{13}=|\mathbf{r}_1-\mathbf{r}_3|\ ;\ r_{23}=|\mathbf{r}_2-\mathbf{r}_3|. \quad (56)$$

Since all molecules are of the same type, $W_i{}^k$ and V_{ik} have the same functional form for every molecular pair, and we may omit the indices i and k. We shall suppose the molecules to be rigid spheres of diameter b, so that when r is less than b, $V(r)$ becomes positively infinite. Attractive forces outside of the sphere a should properly be represented by a potential of the form, $-\gamma/r^6$. However to simplify calculations, we shall represent this potential by a trough of depth u_0 and width, $a-b$. Between the concentric spheres of radii b and a, $V(r)$ is thus equal to $-u_0$. The potential $V(r)$, upon which the following calculations are based is represented by the following step function.

$$\begin{aligned} V(r)&=\infty, && 0\leqslant r\leqslant b\\ &=-u_0, && b\leqslant r\leqslant a\\ &=0, && a<r. \end{aligned} \quad (57)$$

With this potential, the integral on the left-hand side of Eq. (56) may be expressed in terms of the volumes of intersection of spheres of radii a and b.

$$\begin{aligned} W(r)/kT&=V(r)/kT-(N\omega_0/v)J(r),\\ \omega_0&=4\pi b^3/3,\\ J(r)&=\frac{1}{\omega_0}\{\omega_{bb}+2(\omega_{ab}-\omega_{bb})(1-e^{\beta u_0})\\ &\quad+(\omega_{aa}-2\omega_{ab}+\omega_{bb})(1-e^{\beta u_0})^2\}, \end{aligned} \quad (58)$$

where ω_{bb} is volume of intersection of two spheres of equal radii b, ω_{aa} that of two spheres of equal radii a, and ω_{ab} that of two spheres of unequal radii a and b, the distance between the centers of each pair of spheres being r. A simple calculation yields

$$\begin{aligned} \frac{\omega_{bb}}{\omega_0}&=1-3r/4b+\tfrac{1}{16}(r/b)^3\ ;\quad 0<r\leqslant 2b\\ &=0,\quad r>2b\\ \frac{\omega_{aa}}{\omega_0}&=(a/b)^3[1-3r/4a+\tfrac{1}{16}(r/a)^3]\ ;\quad 0<r\leqslant 2a\\ &=0,\quad r>2a\\ \frac{\omega_{ab}}{\omega_0}&=\tfrac{1}{2}\{[1-\tfrac{3}{4}(1-(\alpha/r^2))(r/b)\\ &\quad+\tfrac{1}{16}(1-(\alpha/r^2)^3(r/b)^3]+(a/b)^3\\ &\quad\times[1-\tfrac{3}{4}(1+(\alpha/r^2))(r/a)\\ &\quad+\tfrac{1}{16}(1+(\alpha/r^2))^3(r/a)^3]\}\ ;\\ &\qquad (a^2-b^2)^{\frac{1}{2}}<r\leqslant a+b\\ &=0,\quad r>a+b\ ;\quad \alpha=a^2-b^2. \end{aligned} \quad (59)$$

By means of Eqs. (58) and (59), $W(r)/kT$ may be computed as a function of the ratios, r/b, a/b, $N\omega_0/v$ and u_0/kT. The probability distribution function, which we shall designate by $G(r)$ may then be calculated from the relation $G(r)=e^{-W(r)/kT}$. We note that $N\omega_0$ is equal to eight times the total volume of the molecules,

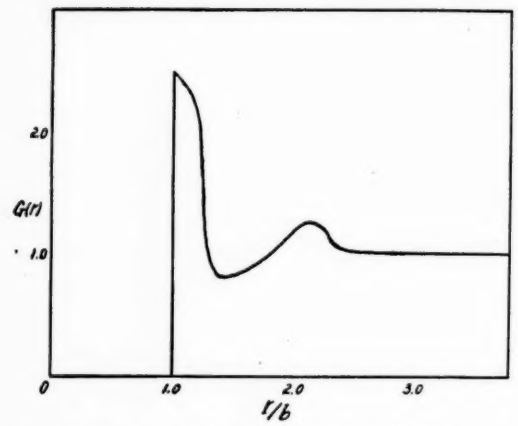

FIG. 1. Molecular pair distribution function based upon Eq. (58).

their radii being $b/2$. For most liquids the ratio $N\omega_0/v$ would have a value between 4 and 6. Moreover, we should expect u_0/kT to be at least unity in liquids. The ratio a/b is somewhat arbitrary. However, in order to make the rectangular trough approximate the actual potential of the attractive forces, which diminishes rapidly with increasing distance, a/b cannot differ much from unity. In order to approach conditions in the liquid state, we assign the following values to the constants in question: $N\omega_0/v=2$; $u_0/kT=1$; $a/b=1.25$. The above value of $N\omega_0/v$ corresponds to a density about a third of ordinary liquid densities. With the above values of the constants, $G(r)$ has been calculated with the aid of Eqs. (58) and (59). It is plotted as a function of r/b in Fig. 1, and tabulated in Table I. Actually there is a discontinuity in the curve at $r/b=1.25$, arising from the artificial nature of the step function potential. In the figure, this discontinuity has been eliminated by drawing a smooth curve through points calculated at r/b intervals of 0.2. It will be observed that the calculated $G(r)$ bears a close resemblance to the molecular distribution functions in liquids derived from measurements of x-ray scattering, exhibiting the characteristic maxima and minima of the empirically determined functions. While we realize that at the temperature and density of the above calculation, the approximation (39) is being pushed to the limit of its applicability, we believe that it adequately illustrates the mechanism by which the intermolecular forces operate to establish molecular pair distribution functions in dense fluids.

TABLE I.

r/b	$G(r)$	r/b	$G(r)$
0.0	0.00	1.6	0.86
0.8	0.00	1.8	0.98
1.0	2.48	2.0	1.20
1.2	2.23	2.2	1.25
1.4	0.81	2.4	1.03
		2.5	1.00

It is interesting to observe that the attractive van der Waals forces play a dominant role in the production of the secondary maximum and minimum in the $G(r)$ of Fig. 1. On the basis of Eq. (39), the distribution function in a fluid of rigid spheres with no attractive forces would exhibit a single maximum at $r=b$. The absence of secondary maxima and minima for rigid spheres is of course the fault of Eq. (39). If the approximation were carried one stage farther, they would begin to appear. However, the point to be emphasized is that probability distribution functions derived from the packing of rigid spheres can scarcely be applied to actual fluids, where the attractive forces play a dominant role in determining the form of the distribution function.

A further limitation of the approximation (39) is that it fails to produce more than a single pair of secondary maxima and minima. For a more exact calculation, it is suggested that the distribution function derived from Eq. (39) be used as a starting point for the self-consistent solution of the more exact integral Eqs. (41) and (42). Thus, it will be observed that tertiary maxima and minima would doubtless arise from the secondary maximum and minimum of the approximate $W(r, \lambda)$ based on Eq. (39), if the latter function were substituted in the integral of Eq. (42). The computational difficulties involved in the self-consistent solution of Eq. (42) are unfortunately rather serious, since even for spherically symmetrical molecules, a triple numerical or mechanical integration is required at each stage of the process. However, these difficulties are not insurmountable.

The formulation of a theory of solutions on the basis of the present ideas offers intriguing possibilities. Several methods of approach are open,

the direct use of our expressions for the chemical potentials being the most obvious. An alternative and more phenomenological treatment applicable to dilute solutions has also been undertaken. These investigations will be described in a future article.

Note added in proof:

(a) A remark about the normalization of the molecular pair distribution functions is perhaps worth while. In defining the potential of mean force, $W_i^k(\lambda_i)$, an arbitrary constant is at our disposal. This constant has been so chosen that

$$(1/v\sigma_k)\int e^{-\beta W_i^k(\lambda_i)}d\omega_k = 1$$

a relation which may be verified by reference to Eq. (20b). The approximate forms for $W_i^k(\lambda_i)$ of course do not exactly satisfy this condition.

(b) At sufficiently high temperatures, the exponentials of Eq. (41) may be expanded and the following approximate linear integral equation is obtained

$$W_i^k(\lambda_i) = \lambda_i V_{ik} - \frac{\lambda_i}{kT}\sum_s \frac{N_s}{v}\frac{1}{\sigma_s}\int V_{is}W_k^s(1)d\omega_s$$

where regions in which W_i^s and W_k^s become infinite due to repulsive forces, are excluded from the integration. If we apply the equation to the ions of an electrolyte solution, the solvent being treated as a continuous medium of dielectric constant D, we know that V_{ik} is equal e_ie_k/Dr_{ik} where e_i and e_k are the ionic charges. For this potential, it may be verified without difficulty that the above set of linear integral equations has the following solutions

$$W_i^k(\lambda_i) = \lambda_i\frac{e_ie_k}{Dr_{ik}}e^{-\kappa r_{ik}}; \qquad \kappa^2 = \frac{4\pi}{DkT}\sum_s \frac{N_s}{v}e_s^2$$

if molecular size is neglected. These solutions, together with Eq. (22) lead to the Debye-Hückel limiting law for the chemical potentials of the ions.

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Some Critical Remarks Concerning Bailli Nilsen's Paper: "On the Theory of Free Radicals and Organo-Alkali Compounds[1]" *

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(Received February 27, 1935)

LATELY, a paper by Bailli Nilsen on the above title appeared in this journal, the main subject of the article being a computation of the electron affinities of free aromatic radicals.

The author first mentions two possible ways of a quantum-mechanical calculation of the electron affinities of such free radicals,—the "first method" certainly alluding to some ordinary first order perturbation method for an atom, or, a molecule when adding an extra electron on an unoccupied orbit—whereas the "second method," as he says, is closely connected with Pauling and Wheland's theory for free radicals.

If now, for instance, we apply such an ordinary perturbation method to the simplest of all atoms, the hydrogen atom, we will find a very poor approximate value of the electron affinity—even the sign being wrong—*viz.*, the negative value -0.25 Rh or -3.385 electron volts—whereas an exact calculation provides a positive value 0.0506 Rh or 0.685 electron volt.

It is true, therefore, that there are many difficulties in determining the energy difference caused by putting an extra electron into an atom or a molecule. We also know that these difficulties are closely connected with considerable changes of the electronic configuration of the atom, because the electron orbits are deformed by the mutual interaction of the electrons. These changes can only be accounted for by the aid of complicated variational methods.

The author of the above paper now seems to be of the opinion that such difficulties may be conquered simply by dropping them out of sight and by making use of the essentially different "second method" of Pauling and Wheland, which is especially suited for quite other purposes, *viz.*, the computation of binding forces between atoms of **given electronic configurations.**

We will, however, quite overlook the considerable errors introduced in this way by neglecting energy changes in the individual atoms themselves, and only analyze the author's application of the "second method."

[1] J. Chem. Phys. **3**, 15 (1935).

* Publikasjoner fra Chr. Michelsens Institutt, Nr. 50.

In Pauling and Wheland's paper electron orbits in individual atoms are designated by letters $a, b, c, \cdots$ and exchange integrals between such orbits by ab, ac, bc, etc. The exchange integrals are, therefore, mathematically well-defined quantities depending only upon the geometrical properties of the supposed electron orbits, which may, for instance, be expressed by some definite kind of eigenfunctions. The values of the integrals have nothing at all to do with the binding electrons occupying those orbits, they only enter into the secular equation of the problem on account of the presence of such electrons.

Now Pauling and Wheland in dealing with the seven-electron problem of the benzyl radical, formally add an eighth electron, called "phantom electron," and a corresponding "phantom orbit" h. Equating to zero all exchange integrals between real orbits and the "phantom orbit" they get a number of singlet terms corresponding exactly to the number of doublet terms of the real problem and with the same energy values.

This procedure may be considered as a purely formal trick, but we may also imagine that it has a definite physical meaning. The "phantom orbit" may well be interpreted as a real electron orbit in a second molecule at some distance which allows the exchange integrals mentioned to be put approximately equal to zero, thus giving qualitatively a picture of a faint, although real and active valence force pointing from the free radical under consideration to some second distant atom or molecule.

In Bailli Nilsen's paper, however, there is no clear distinction between the binding electrons themselves and the possible orbits of the electrons. Sometimes he speaks of exchange integrals between orbits, sometimes between electrons, and he never tries to give a clear definition of the "phantom orbit" introduced. On the contrary he only speaks of the "partner" of the "charging electron" in that or that "canonical structure." Following Pauling and Wheland he assigns definite values to the exchange integrals ab, ac, $\cdots$, bc, bd $\cdots$, between the 7 original orbits, $a, \cdots g$, either the common approximate value α or the approximate value zero according to whether the orbits belong to neighboring atoms or not. In this case he quite correctly takes no account of the direction of the valence forces in various "canonical structures." In the case of the "phantom orbit," however, **he puts the exchange integrals ah, bh, ch, etc., sometimes equal to α and sometimes equal to zero—in the very same secular equation.**

Thus in his matrix element H_{11} we have to add integrals of this kind to the complete expression

$$-\tfrac{1}{2}(ah+bh+ch+dh+eh+fh)+gh$$

and correspondingly in his matrix element H_{35} we get the expression

$$\tfrac{1}{2}[ah+ch-2\,bh-\tfrac{1}{2}(dh+eh+fh+gh)].$$

In the first matrix element H_{11} he now puts $gh=\alpha$, all other integrals equal to zero, whereas in the second element H_{35} he assigns the value α to ah and ch now putting all remaining integrals, including the above gh, equal to zero.

Having completely overlooked the necessity of a "materialization" of the "phantom orbit" he can freely fancy that his "phantom electron" is sometimes here and sometimes there, in the "neighborhood" of this or that "partner."

If it had originally been the author's opinion that the "charging electron" is in some way continually jumping from one atom of the molecule to another, he should, or course, have made use of the available electron orbits, one per atom. Then there would be a different number of orbits and electrons, and the special formal method of "superposition patterns" put forth by Pauling and Wheland could not have been applied at all in the given form. Also in this case, of course, the difficulties of determining the perturbation energy of the individual atoms remain to the same degree.

The conclusion I want to give is, therefore, that in my opinion the whole treatment of the electron affinities of free aromatic radicals as given by Bailli Nilsen is unclear and misleading—and if not thoroughly revised—it must be considered as meaningless.

Remarks on the Theory of Aromatic Free Radicals

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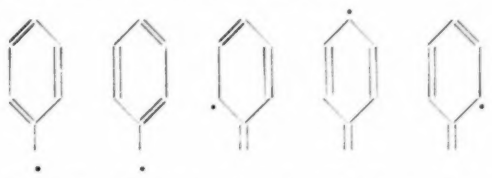
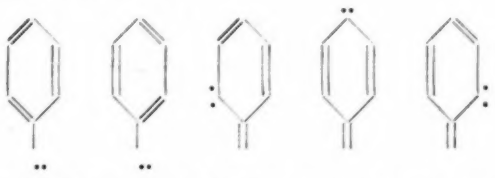
(Received March 5, 1935)

IN the quantum-mechanical treatment of the benzene molecule (and of other aromatic molecules)[1] the approximation is usually made of neglecting the pairs of electrons which are considered to form bonds in the plane of the ring. The problem then becomes one of discussing the wave function which can be constructed for the remaining electrons by use of the p_z orbitals, one for each carbon atom. This discussion can be made either by the molecular orbital method or by the valence bond method, the results being in general agreement. The treatment of a free radical such as phenylmethyl is closely similar, seven p_z orbitals and seven electrons being considered for this molecule. It is found convenient in applying the valence bond method[2] to introduce a "phantom orbital" and an additional electron, a procedure which simplifies the treatment without changing the results.

The quantum-mechanical treatment of the electron affinity of a free radical involves the similar treatment of the negative ion, the wave function for the ion being formed by the use of the same p_z orbitals as for the radical, but with one more electron (eight electrons and seven p_z orbitals for the phenylmethyl negative ion). The discussion of this problem by the molecular orbital method has been given by Wheland,[1] who showed that the electron affinity is approximately equal to the difference in coulomb energy of the ion and radical, the difference in resonance energy being small in all the free radicals. This result is not in disagreement with experiment. The valence bond method can also be applied to this problem. For example, we might consider for the phenylmethyl radical (as an approximation) only the five unexcited structures



in which the dot represents the odd electron (considered bonded to a phantom orbital in our graphical treatment), and for the ion the five unexcited structures



in which the pair of dots represent two electrons (with opposed spins) occupying the same p_z orbital. It is found, however, that the secular equations for the ions involve several integrals which are presumably not small enough to be neglected and for which we have not been able to estimate reliable values; for this reason we have not carried out the calculation. It seems probable, from the form of the canonical structures of radical and ion, that the valence bond method would give essentially the same result as the molecular orbital method, namely, that the difference in resonance energy of radical and ion is small.

The attempted application of the valence bond method in the calculation of the electron affinities of free radicals made by Nilsen[3] is criticized by Hylleraas in the preceding paper.[4] We agree with Hylleraas that Nilsen has not correctly evaluated the resonance energy, and in addition we point out that he has neglected to mention the changed coulomb energy, which in our opinion is the major contributor to the electron affinity.

[1] E. Huckel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); **76**, 628 (1932); **83**, 632 (1933); L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933); L. Pauling and J. Sherman, ibid. **1**, 679 (1933); G. W. Wheland, ibid. **2**, 474 (1934).

[2] L. Pauling, J. Chem. Phys. **1**, 280 (1933). Cf. also L. Pauling and G. W. Wheland, reference 1.

[3] B. Nilsen, J. Chem. Phys. **3**, 15 (1935).

[4] E. A. Hylleraas, J. Chem. Phys. **3**, 313 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Isotope Ratio in Petroleum

The natural separation of isotopes of hydrogen in benzene and kerosene found by M. Dole[1] was called in question by the author himself because of later experiments with benzene (under modified conditions).[2] The results of his initial experiments were explained by him as a consequence of fractional condensation of water vapors from the products of combustion.

I burned the motor-petroleum from Machach-Kala in a calorimetric bomb, so that the possibility of fractional condensation was excluded. All the water obtained was subjected to an elaborate purification. The interferometric analysis gave 1.5 parts deuterium per 5000 parts of hydrogen for the concentration of deuterium in petroleum if, as usually, the mole fraction of the former in ordinary distilled water is taken as 1 : 5000. If the tank oxygen used for the combustion has an increased concentration of heavy oxygen isotopes (as it was found by Smith[3]), then according to Luten[4] this would decrease the value of Δn, i.e., the ratio 1.5 : 5000 for concentration of deuterium in investigated motor-petroleum is decreased.

I wish to express my sincere gratitude to Professor Dr. A. E. Brodski for suggesting this work and for his valuable advice.

N. S. FILIPPOVA

Institute of Chemical Technology,
Dniepropetrovsk, U.S.S.R.,
February 25, 1935.

[1] M. Dole, J. Chem. Phys. **2**, 337 (1934).
[2] M. Dole, J. Chem. Phys. **2**, 548 (1934).
[3] E. R. Smith, J. Chem. Phys. **2**, 298 (1934).
[4] D. B. Luten, Phys. Rev. **45**, 161 (1934).

The Intensities of the Vibration-Rotation Bands of HCl

The writer's attention has recently been called to Professor Mulliken's *Note on Electric Moments and Infrared Spectra* and to the subsequent note of correction.[1] In his second communication Mulliken takes cognizance of the recent intensity measurements of Bartholomé on the 0→1 bands of HCl, HBr and HI, and of the serious discrepancy between the results obtained by Bartholomé and those previously obtained by Bourgin.[2] Mulliken accepts at its face value Bartholomé's argument in favor of the superiority of his method and combines the Bartholomé result for the 0→1 band of HCl with that of Dunham[3] for the 0→2 band to derive a pair of alternative values for the coefficient of the quadratic term of the expansion of the electric moment ρ in powers of the vibrational displacement.

Since the measurements of Bourgin and Dunham were both carried out by the same method under the general supervision of the writer, some comment on the validity of their conclusions is, perhaps, in order. The method consists in the observation of the areas A under the absorption curves (measured in percent) of the individual band lines for a variety of tube-lengths x. The initial slope of this curve $(dA/dx)_0$ is the integrated absorption coefficient α for the corresponding line. The criticism's of the method made by Bartholomé are (a) that there may be some surface absorption due to adsorbed vapor on the end plates of the absorption tube, and (b) that there must be a very large probable error in the determination of the initial slope of the A, x curve in view of the marked curvature in the neighborhood of the origin. In the writer's opinion these criticisms are wholly inadequate to account for the discrepancy between Bourgin's result and Bartholomé's.

According to Bartholomé the true intensity of the 0→1 band should be only one-fourth of that observed by Bourgin. This discrepancy factor is subject to a correction even if we grant for the moment the validity of Bartholomé's method and results. In his second paper Bourgin re-estimated the initial slope of the A, x curve by several methods and corrected numerical errors in the previously published computations of the transition probabilities and effective electric moment of the molecule. The most probable value of the absolute integrated absorption coefficient obtained by averaging the results of four methods given in the second paper is 41×10^{10} instead of the value 49×10^{10} given in his first paper. The corresponding value of the Einstein transition probability for the first line of the R branch is[4] 8.6×10^{15}. This transition probability, which we denote by $B_{01}{}^{+1}$, is to be distinguished from the average transition probability for the entire band $(\overline{B_{01}})$ observed by Bartholomé. These two quantities would be the same according to the summation rules if the frequency differences between the different band lines were negligible. Assuming the theoretical formula for the relative intensities of the band lines derived by the writer and confirmed within the limits of experimental error by Bourgin, calculation indicates that at 20°C $B_{01}{}^{+1}=0.96\overline{B_{01}}$. From Bartholomé's value of $\overline{B_{01}}$ we obtain $(B_{01}{}^{+})_{\text{Barth.}}=1.83\times10^{15}$, or approximately 21 percent of Bourgin's

value. Thus the use of Bourgin's revised figures together with the application of the above correction factor slightly increases the discrepancy previously noted.

Let us now return to the criticisms of Bourgin's method. As regards adsorbed vapor, one may note that the vapor pressure of HCl at room temperature is about 45 atmospheres. Since the pressure of the gas actually used was one atmosphere, one may reasonably assume that the adsorbed layer would not be much more than one molecule deep. Taking the cross section of the molecule standing on end to be 10^{-16} sq. cm, one readily calculates that the number of adsorbed molecules per square centimeter on the front and back quartz surfaces is equal to the number per sq. cm in a layer of gas less than a hundredth of a millimeter thick. Even if the adsorbed molecules were free to rotate normally and contribute as much to the absorption as free molecules, their contribution would have been too small to detect experimentally. Moreover, the base-line readings were taken without removing the adsorbed gas by heating, so that most of its contribution to the absorption must have been eliminated by subtraction.

Finally an examination of the A, x curves (cf. Fig. 4 in the first paper and Fig. 1 of the second paper) should make it evident that Bourgin's estimate that the extrapolated value of the initial slope is reliable within 20 percent, is a fair one. These estimates were made with the aid of two-parameter semitheoretical curves which were fitted to the complete absorption curve and gave due weight to the observations made with long tubes. In fact we can derive from the A, x curves a lower bound to the value of $B_{01}{}^{+1}$ which is several times as large as that given by Bartholomé. From the fundamental formula for the area, *viz.*, $A(x) = \int(1-e^{-\mu x})d\nu$, it follows that $dA/dx = \int \mu(\nu)e^{-\mu x}d\nu$. Hence dA/dx and all the higher derivatives of $A(x)$ are monotonically decreasing functions of x. It follows that *the initial slope must be greater than the slope of any chord connecting two points on the curve.* Joining the origin with the points for the two shortest tubes and using the data for the third line of the R branch (the strongest in the band) one obtains the lower bounds 7.05×10^{15} and 5.84×10^{15} for $B_{01}{}^{+1}$. The other lines yield similar bounds. Thus it is quite impossible to reconcile Bourgin's data with Bartholomé's low value of the transition probability.

Let us next consider the possibility of error in Bartholomé's experiment. The observations consisted in measuring the absorption with a relatively wide spectrometer slit and an absorption tube containing one atmosphere of HCl mixed with air at total pressures up to 60 atmospheres. The theory of the experiment is that at sufficiently high pressures the lines will be broadened enough to destroy the rotational structure of the band and give a smooth curve for the absorption coefficient plotted against frequency. Under these circumstances with a slit-width small enough to cover one line at a time, but not necessarily small enough to resolve rotational structure, the radiation reaching the radiometer should be sensibly homogeneous as regards its absorption coefficient. By means of the exponential absorption law it should then be possible to determine the smeared-out absorption coefficient curve from observations made with a single tube-length. It is assumed that the transition probability is sensibly independent of the pressure and on that point the evidence is reasonably conclusive.

It is rather difficult and dangerous to criticize an experiment from as meager an account of the experimental details and data as that given by Bartholomé, but one weak point is apparent. He gives his slit width as equivalent to 800A. If we assume that the entrance and exit slits of the spectrometer were of equal width, as is customary in such work, the extreme range of wavelengths reaching the thermopile would be 1600A. As the distance between the points of maximum intensity for the R and P branches is about 1400A, it is quite clear that even when the lines were broadened so as to eliminate the rotational fine structure, the radiation reaching the microradiometer must have been very inhomogeneous as regards its absorption coefficient. In the R branch for example, the 4th line has an intensity five times as great as the 8th line which differs in wavelength by only 750A. Thus it is not permissible to extrapolate to zero tube-length by means of the exponential absorption law and an attempt to determine the transition probability by means of such an extrapolation is sure to underestimate seriously its true value. With higher resolving power Bartholomé's method should be good.

EDWIN C. KEMBLE

Harvard University,
Research Laboratory of Physics,
March 27, 1935.

[1] R. S. Mulliken, J. Chem. Phys. **2**, 400, 712 (1934).
[2] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).
[3] J. L. Dunham, Phys. Rev. **34**, 438 (1929).
[4] The value given in Bourgin's first paper was wrong by a factor of two.

Active Hydrogen

Four years ago I expressed my doubts in what at that time was considered to be proofs for the existence of triatomic hydrogen.[1] It appeared that a final decision had been reached when Conrad in his mass-spectrographical work[2] found an uncharged molecule corresponding to the mass (3). Unfortunately the significance of his investigation was greatly reduced[3] after deuterium was discovered. A strict distinction should be made between HD and H^3 even in mass-spectrograph analysis. This has not been done in every case.[4] Hence positive ray analysis as applied to this problem must take account of the two facts, (1) that the presence of HD may obliterate an unequivocal decision, (2) that only such particles[5] can be considered as a proof of H^3 which were uncharged for some definite length of time and received their charge later on by electron transfer.

The H^3 molecule may have properties identical with those of the H-atom. One would have to assume this, reading the publications of Grubb and co-workers[6] if their argumentations were conclusive in every respect. Only their most weighty argument of their most recent publica-

tion may be considered. Either the decay reaction occurs independently of the surface or their wall reaction is erroneous. Both cannot be assumed at the same time. Conceding for a moment that the wall reaction be negligible, a homogeneous gas reaction of the first order is improbable because it will be difficult to suggest a mechanism which would fit such an assumption. A monomolecular decay should therefore be explained as a wall reaction. It seems possible[7] to oppress this wall reaction even more than Steiner and Wicke[8] were able to do. One may argue that active hydrogen in as small a concentration as 0.001 to 0.025 percent[9] would have exactly the same properties if explained on the basis of the well-known atomic modification. This argumentation may be followed up in every instance.

Wrede's orifice method[10] and Keussler's study of the absorption spectrum of H-atoms[11] would be sufficient proof to substantiate the atomic nature of that hydrogen which is obtained by Wood's method, unless the bulk of other investigations which were based on this assumption is taken as proof in itself. A decision in favor of H^3 appears exceedingly difficult by the use of merely chemical methods.

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Universität Berlin (Germany),
Physikalisch-chemisches Institut,
April 15, 1935.

[1] J. Phys. Chem. **35**, 3186 (1931).
[2] Zeits. Physik **75**, 504 (1932); Zeits. f. Electrochemie **38**, 183 (1932).
[3] Zeits. f. physik Chemie **A164**, 30 (1933); Cf. Ann. d. Physik [5] **8**, 456 (1931).
[4] Grubb, Nature **132**, 1001 (1933); J. J. Thompson, Nature **133**, 280 (1934). Cf. Phil. Mag. **17**, 1025 (1934).
[5] O. Luhr, J. Chem. Phys. **3**, 146 (1935); Zeemann and Gier, Proc. Amst. Acad. **36**, 717 (1933). Cf. Bainbridge, Phys. Rev. **44**, 57 (1933). Massey, Proc. Camb. Phil. Soc. **27**, 451 (1931). Zentr.-bl. 1932, I, 636.
[6] J. Chem. Phys. **3**, 139 (1935); Nature **132**, 1001 (1933); J. Phys. Chem. **36**, 2817 (1932).
[7] Amdur and Robinson, Phys. Rev. **43**, 208 (1933); J. Am. Chem. Soc. **55**, 1395, 2115 (1933).
[8] Zeits. f. physik. Chemie, Bodenstein Festband 817 (1931). Cf. Wartenberg and Schultze, ibid. **B6**, 261 (1929).
[9] Grubb, reference 4.
[10] Zeits. f. Physik **54**, 53 (1929).
[11] Ann. d. Physik [5] **7**, 225 (1930).